

**ROLE OF BANK MATERIALS AS POTENTIAL SOURCE AND CARRIER OF
PHOSPHORUS**

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Ashley Lynn Grundtner

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Satish C. Gupta, ADVISER

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Abstract

Lake Pepin is a natural impoundment on the Upper Mississippi River, 80 km south of the Twin Cities, Minnesota. Two major water quality concerns for this lake are the higher rates of sedimentation and elevated eutrophic nutrient conditions. Although the majority of sediments in the Minnesota River and then Lake Pepin are coming from river banks, there is a perception that a significant amount of particulate phosphorus is coming from agricultural lands. The goal of this research was to assess the role of river bank materials as a source and carriers of phosphorus to Lake Pepin. In this study, we characterized the river bank materials in Blue Earth County for equilibrium phosphorus concentration (EPC_0), total phosphorus (TP) content, particulate bound P fractions, and the potential of bank materials to adsorb and desorb soluble P. Results showed that bank materials are inherently high in TP content (>400 mg/kg), have low EPC_0 (<0.1 mg/L) values, strong P binding ability, and high P adsorption and low P desorption potentials. Since the dissolved P concentrations in river waters contributing to Lake Pepin are >0.1 mg P/L part of the year, low EPC_0 values suggest continued P adsorption by bank materials from river waters even under current conditions. Particle enrichment of bank materials during transport explained TP concentrations in Lake Pepin sediments prior to 1850. After 1850, we outlined scenarios using particle enrichment and historical river pollution as potential reasons for higher TP concentrations in Lake Pepin sediments. We conclude that river bank materials are a significant source of TP but not that of dissolved P to either the river system or to Lake Pepin. These materials do act as scavengers of dissolved P from river waters and carry it to downstream locations. The dissolved P in the river could be from the treatment plants, some point sources or agricultural lands. This adsorbed P will be stored in locations where sediments settle and will be a continuous source of dissolved P in the future. One way to prevent sediment from semi-sequestering dissolved P from river waters is to make sure dissolved P concentrations in river water are less than EPC_0 values of bank materials.

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List of Abbreviations

Al- Aluminum
Ca- Calcium
cfs- Cubic feet per second
DOP- Dissolved Organic Phosphorus
DRP - Dissolved Reactive Orthophosphate
DNR-Department of Natural Resources
EDA-Elevation Derivative Applications
Fe - Iron
GBERB- Greater Blue Earth River Basin
ka BP- Year in thousands Before Present
LiDAR- Light Detection and Ranging
LTRMP-Long Term Resource Monitoring Program
MCES-Metropolitan Council of Environmental Services
OM -Organic Matter
PP- Particulate Phosphorus
P-Phosphorus
RM -River Mile
SRP - Soluble Reactive Phosphorus
STORET-STORAge and RETrieval
STP - Sewage Treatment Plant
TMDL - Total Maximum Daily Load
TP-Total Phosphorus
TSS- Total Suspended Solids

“No one has a right to use America’s rivers and America’s waterways that belong to all the people as a sewer. The banks of a river may belong to one man or one industry or one state, but the waters which flow between those banks should belong to all the people” **President Lyndon B. Johnson.**

Introduction

Nature of the Problem

Lake Pepin, a natural impoundment on the Upper Mississippi River bordering Minnesota and Wisconsin, is located about 80 km southeast of the Minneapolis-St. Paul metropolitan area. Following the retreat of the Laurentide Ice Sheet, the lake was formed when an alluvium fan of the Chippewa River blocked the Mississippi River at their confluence. Since the Chippewa River had a steep gradient (0.6 m per km) and a high level of coarse material, the Mississippi River could not remove the excess sediment from the alluvium fan which led to the damming of the Mississippi River and forming of a large impoundment called Lake Pepin (Zumberge, 1952; McHenry et al., 1980; Wright et al., 1998).

Originally the lake extended upstream as far as St. Paul, MN. However, subsequent infilling by sediments has reduced the length and volume of the lake and thus shifted the headwaters of the lake 80 km downstream to Redwing, MN (Zumberge, 1952).

Schoolcraft (1855) noted the presence of a delta in the Mississippi River upstream of Lake Pepin in 1832. For the period 5.2 to 1.5 ka BP, Blumentritt et al. (2009) estimated the delta migration rate of 7.7- 12.8 m per year. The delta migration, along with sediment settling, has reduced the volume of Lake Pepin. Today the lake is 34 km long and has a mean depth of 5.4 meters, a surface area of 103 km² and a gradient of about 5 cm per kilometer (McHenry et al., 1980; Engstrom et al., 2009). Due to the low gradient and deeper water depth, the lake acts as a settling pond and has accumulated over 10,000 years of fine-grained sediments and nutrients. Based on the paleolimnological data, Engstrom et al. (2009) suggested that the rate of lake infilling has accelerated with the current rate being 10 times higher than the pre- European settlement rate.

Besides Lake Pepin infilling there are also additional water quality concerns in terms of major ions which result in degraded ecosystems. In the summer of 1988, an unprecedented blue-green algae bloom caused a massive fish kill in Lake Pepin (Heiskary and Vavrck, 1993; Larson et al., 2002). During that summer, the mean flow in the Mississippi River upstream of Lake Pepin was 4,910 cubic feet per second (cfs) and the

mean water resident time was 46 days (Larson et al., 2002). Sediment attached phosphorus was identified as the major reason for algal bloom (Heiskary and Vavricka, 1993). Phosphorus (P) acts as a limiting nutrient in freshwater systems and excess levels lead to dense growth of biomass known as eutrophication. During subsequent decomposition of this biomass there is a depletion of dissolved oxygen in the water column which leads to fish kills (Caraco, 2009).

Lake Pepin sediment cores taken by Engstrom et al. (2009) showed that prior to 1850 the total phosphorus concentration ranged from 600-800 mg/kg. This concentration continued increasing over time with a peak value of 1800 mg/kg from 1950-1980. On an average, total phosphorus (TP) concentrations in recent decades are roughly 2 times more than those in pre-settlement times (Engstrom et al., 2009). A majority of the TP in Lake Pepin sediments is comprised of inorganic P with concentrations varying from 500-700 mg/kg prior to 1850 and an average peak value of 1300 mg/kg from 1950-1980. Total P and turbidity levels in Lake Pepin currently exceed the proposed Total Maximum Daily Load (TMDL) standards and the lake is listed on the Minnesota Impaired Water List (303d List) for eutrophic nutrient levels.

Lake Pepin Watershed Area

The sediments and nutrients in Lake Pepin are supplied by three major rivers and a few minor tributaries draining a 122,000 km² watershed encompassing Minnesota, Wisconsin and South Dakota. These three major rivers are the headwaters of the Mississippi River, the Minnesota River, and the St. Croix River. The Upper Mississippi River above Lake Pepin runs roughly 850 river kilometers, from its headwaters in Itasca State Park in northern Minnesota, before it is joined by the Minnesota and the St. Croix Rivers near St. Paul, MN, and Hasting, MN, respectively.

The Upper Mississippi River drains roughly 56,600 km² of the watershed and contributes 50% of the flow and 26% of the TP to Lake Pepin (Engstrom and Almendinger, 2002). Soils in the Upper Mississippi River are mainly Alfisols (52%) derived from non-calcareous glacial tills with some area under fine textured Mollisols (21%), and coarse textured Entisols (15%). The landscape of the basin is forest dominated (39%), with the

remaining area under agriculture (33%), wetlands (10%), urban development (6%), and pastures (3%) (USDA, 2006; USDA, 2008).

The Minnesota River joins the Mississippi River at Fort Snelling where it contributes 25% of the flow, 32% of the TP, and 75% of the total suspended solids (TSS) (Engstrom and Almendinger, 2002). The Minnesota River watershed drains 43,400 km² of the area covering western Minnesota and a small part of eastern South Dakota. The soils in the basin are mainly fine textured Mollisols (89%) derived from calcareous glacial tills. About 75% of the area is under agriculture with about 8% under pastures, 6% urban lands, and 5% wetlands (USDA, 2006; USDA, 2008). The Minnesota River was formed when the Laurentide Ice Sheet retreated and the enormous glacial Lake Agassiz drained through a southern outlet named River Warren. Reaching the exposed limestone bedrock in south central Minnesota the water was buffeted northward; creating a unique “V” shaped river path that eventually met the Mississippi River south of current day Fort Snelling in St. Paul, MN. After the Lake Agassiz southern outlet dried up, River Warren was replaced by the smaller flowing Minnesota River. Today the Minnesota River flows through the much larger River Warren floodplain (Kelley et al., 2006).

The St. Croix River drains 22,000 km² of eastern Minnesota and northwestern Wisconsin through mainly Superior lobe bedrock. The basin is dominated with Alfisols (48%) derived from non-calcareous glacial tills and the remaining area is divided between Sposodsols (28%), Inceptisols (10%), Histosols (8%), and Entisols (3%). Much of the land consists of forest (55%) with some area under agriculture (24%), wetlands (10%), and urban development (4%) (USDA, 2006; USDA, 2008). The original landscape was heavily White Pine forests that were logged from 1839 to around 1900. The St. Croix River is one of the original eight US waterways in the 1968 National Wild and Scenic River Act. The river is nearly pristine, relative to other major Midwestern rivers. In 2008, the St. Croix River was listed on the Minnesota 303d impaired waters list due to high P levels. Today the St. Croix River provides 25% of the flow and about 4% of the average TP to the Upper Mississippi River at their confluence in Hastings, MN (Engstrom and Almendinger, 2002; Edlund et al., 2009).

Based on trace metals in silt, Kelley et al. (2006) estimated that at least 75% of the sediments in Lake Pepin originate from the Minnesota River Basin and several counties in southeastern Minnesota between St. Paul and Lake Pepin. Meyer and Schellhass (2002) estimated that the TSS transported by the Minnesota River at Fort Snelling was as much as 623,000 Mg per year, or 95 truckloads each weighing 18 Mg per day.

Greater Blue Earth River Basin (GBERB) is located in southern Minnesota and northern Iowa and includes three major watersheds; the Blue Earth River watershed, the Le Sueur River watershed, and the Watonwan River watershed (Fig. 1). This basin is a relatively flat with deeply incised streams that are lined with steep and unstable banks that reach heights over 50 meters (Fig. 2). At the confluence of the Minnesota River and the Greater Blue Earth River in Mankato, as much as 46% of the water flow and 55% of the sediment originate from the GBERB (Payne, 1994).

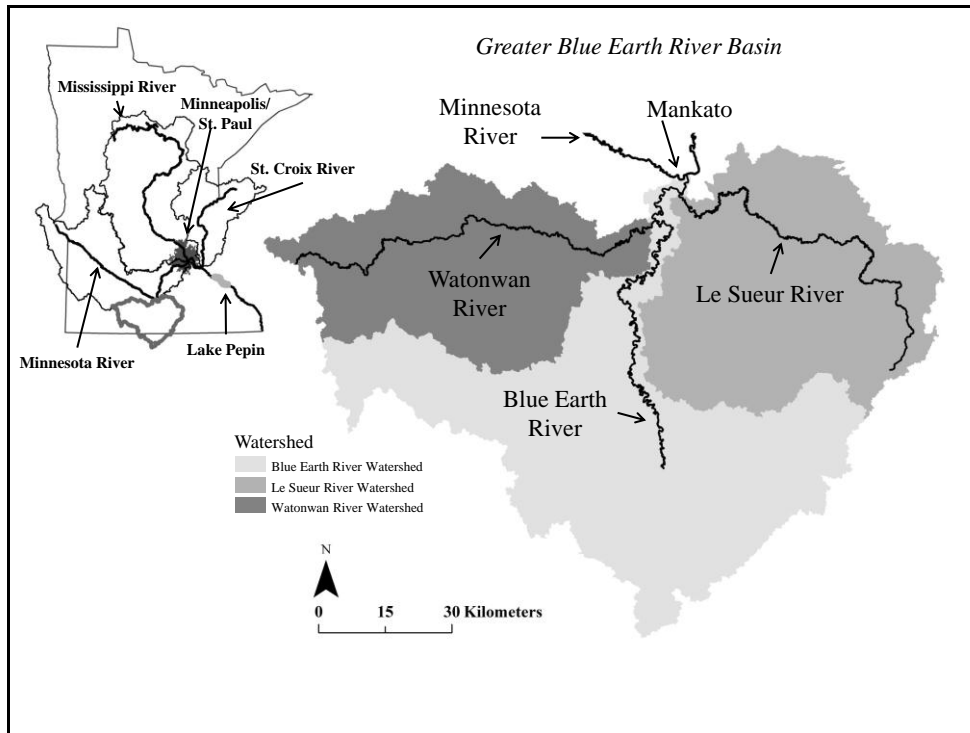


Figure 1. Map of Minnesota showing the Minnesota River, the Mississippi River, and the St. Croix River watersheds. Also, shown are the Greater Blue Earth River Basin (GBERB) and its sub watersheds.



Figure 2. Typical river bluff in GBERB. Person at the base of the bank is for scale.

The GBERB covers approximately 2.3 million acres with 54% of the land having less than 2% slope and 93% of the land less than 6% slope. Within the basin the landscape is primarily (88%) used for agricultural purposes with most area under row crops (Davis and Rofshus, 2012). Figures 3 through 5 show the land use breakdown in three major watersheds of GBERB: the Blue Earth River, the Le Sueur River, and the Watonwan River watersheds. Although an intensely cultivated landscape there is a strong conservation mindset, which is reflected in the percentage of land in conservation tillage, 42% within the Blue Earth River watershed, 38% in the Le Sueur River watershed, and 30% in the Watonwan watershed (Tetra Tech, 2009). The soils in the GBERB are mostly composed of moraines, glacial till, glacial lake beds, and some lacustrine and alluvium. Calcareous glacial till is the most prevalent parent material in the basin (Fang et al., 2005).

Blue Earth River- Existing Land Use

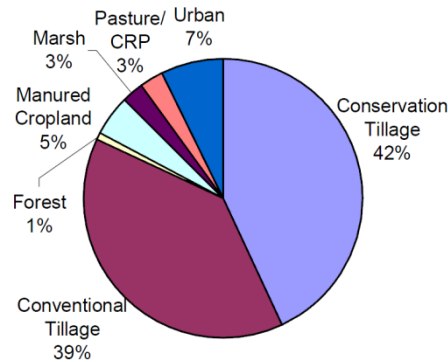


Figure 3. Existing land use in the Blue Earth River watershed (Tetra Tech, 2009).

LeSueur River- Existing Land Use

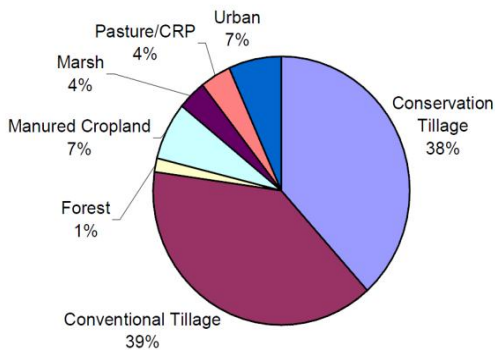


Figure 4. Existing land use in the Le Sueur River watershed (Tetra Tech, 2009).

Watonwan River- Existing Land Use

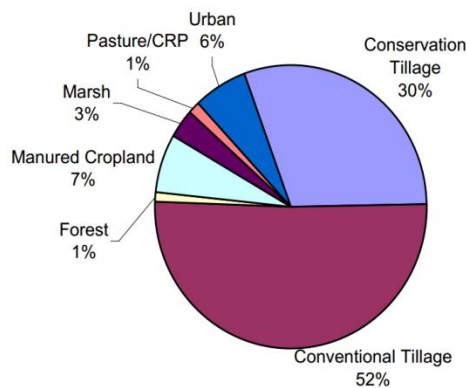


Figure 5. Existing land use in the Watonwan River watershed (Tetra Tech, 2009).

The settled sediments in a water body, such as Lake Pepin, also record the environmental conditions the lake may have experienced in the past. The discipline dealing with the analysis of this stored sediment is called paleolimnology and has been used by

paleolimnologists to reconstruct paleoenvironments of lakes, including past water quality (Smol, 2009). Based on the pollen analysis in sediment cores from Lake Pepin, Engstrom et al. (2009) suggested that cultivation of native prairie landscape to agriculture in the Minnesota River Basin is the primary reason for the increased sedimentation rate in Lake Pepin starting around 1830. Since there has also been substantial re-plumbing of the landscape starting in 1910, Engstrom et al. (2009) further suggested that hydrologic alteration was another potential reason for increased sedimentation in Lake Pepin. The hydrologic alterations included draining wetlands, connecting previously closed basins to the drainage network, ditching small tributaries, and tiling agricultural fields to ensure rapid drainage of surface and vadose zone water (Gran et al., 2009). The tilling and other landscape alterations have been hypothesized to rapidly move the water away from the landscape thus increasing river flows as well as transporting additional sediments downstream to Lake Pepin.

Since the GBERB is a relatively flat basin (54% of the land having less than 2% slope and 93% of the land less than 6% slope), some researchers (Thoma et al., 2005; Gupta et al., 2011) have suggested that agricultural fields could not be the major source of sediments to the Minnesota River and Lake Pepin. These authors reasoned that a steep landscape is needed to transport field eroded soil to the rivers and that is largely missing in the Minnesota River Basin, including the GBERB. Gupta et al. (2011) further noted that earlier settlers' ploughs were primitive, did not cultivate deep, and thus would not have caused large scale soil disturbance and erosion. Other significant facts included the limited number of settlers (6,077) in Minnesota in 1850 and most of the settlers were living near the Twin Cities (Dole and Wesbrook, 1907). Also, most wetlands were not drained prior to 1910 because wild hay, which grew near these wetlands, was used for the draft animals (Burns, 1954; Moline, 1969).

Recently, stream flow analysis has also shown that annual water balance has not changed drastically since 1910 (Gupta et al., 2012). For a given level of annual precipitation, river flows are nearly similar for the periods prior to 1975 and after 1976. The breakpoint of 1975 corresponds to the period since when plastic tile line was routinely used for tile

drainage in northern states. Due to this routine use, there has been a significant increase in the area under tile drainage through the replacement of degraded old clay and cement tiles, close spacing of existing tiles, and drainage of new areas. This flow analysis further suggested that increased river flows which have been construed as signs of altered hydrology, are in fact the result of increased precipitation in recent years (Gupta et al., 2012). This combined evidence of limited number of people in the Minnesota River Basin in 1830, primitive plowing technology and need to use wild hay for draft animals in earlier European settlement times, and increased precipitation in recent times would suggest that cultivation and drainage of agricultural fields could not be the major reasons for increased rates of sedimentation seen in Lake Pepin starting in 1830. Based on the observations that many rivers in GBERB and the Minnesota River Basin are lined with steep- unstable banks that reach heights over 50 meters and many of these banks were bare (indication of active sloughing), Gupta and Singh (1996) suggested that river banks are likely the major source of sediments in the Minnesota River and then in Lake Pepin.

Bank Material Source Concept

Several studies have reported on stream bank contributions to TSS and TP in rivers. Odgaard (1987) estimated that bank erosion contributes between 30% to 40% of the sediments in the East Nishnabotna and Des Moines Rivers in Iowa. Using erosion pins, Bauer (1998) estimated that stream bank slumping accounted for 36% to 84% of the TSS load in the Blue Earth River. Based on successive topographic data, Sekely et al. (2002) found that bank slumping accounts for 31% to 44% of the annual sediment and 7% to 10% of the annual TP load in the Blue Earth River. The TP losses associated with sediment loading were estimated based on average soil TP concentration of 441 mg/kg derived from sixteen samples. Both Bauer and Sekely's data was based on one year of measurements on seven river banks. Sekely et al. (2002) extrapolated this data to the whole length of the river using the river bank area as a surrogate variable. Since bank slumping processes vary from bank to bank and every bank does not slump each year, extrapolation of limited data based on area as a surrogate variable to whole river reach was inappropriate.

Recent technology has made it possible to overcome the limitations associated with extrapolation of limited slumping data to the rest of the reach. Thoma et al. (2003) used airborne Light Detection And Ranging (LiDAR) on 56 km of the Blue Earth River to characterize sediment and phosphorus contributions from river bank erosion. The mass wasting estimates from 2001-2002 varied from 23% to 56% of the sediment mass transported past the gauging station. Associated TP contributions were estimated at 201 tons per year. Using the airborne LiDAR technology, Kessler et al. (2012) conducted a similar analysis on bank slumping as that of Thoma et al. (2003) but for the full length of several rivers in Blue Earth County, MN. The analysis showed that bank erosion contributed as much as 48% to 79% of the TSS measured at the mouth of the Blue Earth River and the Le Sueur River in 2005-2009. Corresponding soluble P and TP contributions ranged from 0.13-0.2% and 40-49%, respectively. Within this 4 year period, the Greater Blue Earth River (after its confluence with the Le Sueur River), contributed 305,880 metric tons per year of river bank material to the Minnesota River at Mankato (Kessler et al., 2012).

The mechanisms causing the slumping of the river banks are currently being researched by various investigators with two main hypotheses. The first is that the bank slumping is linked to natural processes such as seepage, sapping, freezing and thawing, and the migration of rivers due to flooding from high rainfall events or from ice jams during early spring (Gupta and Kessler, 2011). The alternative hypothesis suggested by St. Croix Watershed Research Station and adopted by MPCA and other state agencies is that the increased tile drainage has increased storm and base flows resulting in increased undercutting of the banks (Ulrich et al., 2010; MPCA, 2012b).

With recent research on bank erosion there is increased consensus among scientific community that the main source of sediments in rivers of GBERB and MRB are the deeply incised river banks. This leads to new questions on the role of river bank materials as a source and as a carrier of P to Lake Pepin and how river/lake dynamic might affect sediment attached P?

This focus of this thesis is on P adsorption and desorption behavior of stream bank materials once they come in contact with river waters. The goal of this research is to address the issues: 1. whether river bank materials are inherently a significant source of P in the Minnesota River /Lake Pepin?, and 2. what is the potential of bank materials from Blue Earth County to adsorb P from river waters?

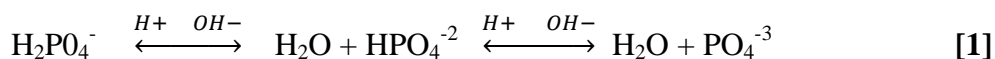
Specific objectives include:

1. Characterization of phosphorus adsorption by river bank materials of various origins in Blue Earth County.
2. Potential of these materials to adsorb P from river waters at historic and current soluble P concentrations.
3. Assessment of river bank materials as the carrier and then source of soluble P in Lake Pepin based on historic river pollution and river bank material adsorption characteristics.

Literature Review

Chemical and Physical P Forms

Phosphorus is a somewhat unique element in that it is an essential element needed for plant growth, it has low solubility, and is not toxic itself; but different concentrations can have detrimental effects on the environment (Randall, 1998). Phosphate was discovered in the 16th century by the German alchemist Henning Brand. Phosphates are the naturally occurring form of the element phosphorus, P. Within the United States it is primarily mined in North Carolina and Florida as rock phosphate. Besides the most common form of PO_4^{-3} , the other common species of P ions are: HPO_4^{-2} , $\text{H}_2\text{PO}_4^{-1}$ and H_3PO_4 (Brady and Weil, 1998). The dominance of specific P ionic specie largely depends upon the solution pH and as the soil pH changes so does the dominance. Equation 1 and Fig. 6 show this change in the dominance of various P species as a function of pH.



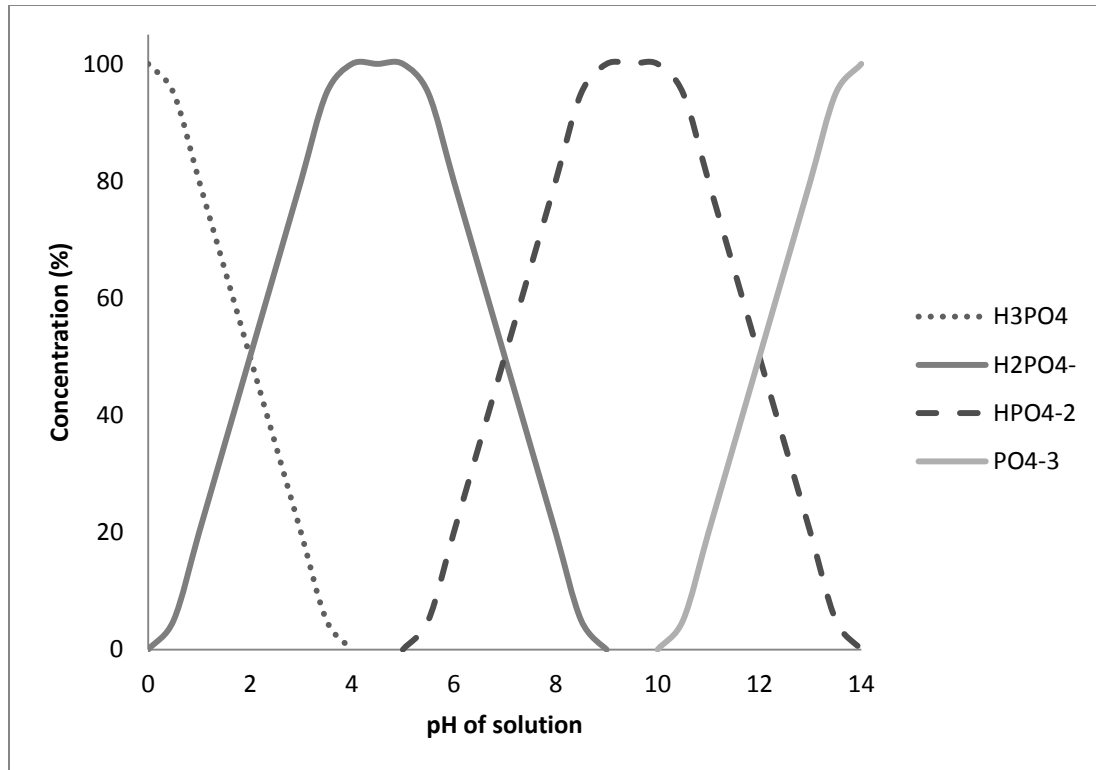


Figure 6. Concentrations of P ionic species as a function of pH. In neutral soils there is an equal amount of HPO_4^{-2} , $\text{H}_2\text{PO}_4^{-1}$ (after Brady and Weil, 1998).

As mentioned earlier, P is an essential element for plant growth but is often limiting in freshwater systems. Unlike nitrogen, oxygen, or many other essential elements, P does not easily convert into vapors and thus has only a minor existence in gaseous phase. In other words, P is a persistent chemical. Furthermore, its' cycling and sequestration in the environment makes it a persistent pollutant of concern (Caraco, 2009). Even though P appears very stable it does have a complex aquatic and terrestrial cycle. In order to understand the fate and transport of the P ion at a watershed scale, it is important to understand the various P forms, mechanisms of their transport, and the many physical, chemical and biological factors that influence this transport.

Phosphorus has two major physical pools: dissolved and particulate phosphorus (PP). The sum of these pools is TP. These pools can be further divided into sub groups. The sub groups of P that are important from the water quality perspective are: organic and

inorganic phosphorus, and labile and refractory phosphorus. There is often some confusion in the scientific literature on the reported P forms. In order to combat this confusion, federal and state agencies often use TP as the basis for policy development (Sterner, 2011). During the summer of 1988 when fish kills occurred in Lake Pepin, mean TP concentration in the lake was 0.46 mg/L (Larson et al., 2002).

For the purposes of this study ortho, soluble, dissolved reactive orthophosphate (DRP), dissolved organic P (DOP) plus dissolved inorganic P are described as soluble reactive phosphorus (SRP). Since SRP is measured on water samples that have passed through 0.45 μm , it also includes <0.45 μm labile organic and particulate P (Kovar and Pierzynski, 2009). From the perspective of water quality standards, it is the SRP which is most detrimental since it is most readily available for algal growth (Larson et al., 2002). The next important P is the inorganic particulate phosphorus (PP) (sediment attached phosphorus) because it acts as a continuous source of available P in lakes and rivers.

In terms of inorganic PP, the P may be attached or bound to other elements. On soil particle, P may be attached to elements such as calcium (Ca), iron (Fe), or aluminum (Al). In geologic material, P may be present as bound P with other elements in minerals. For example in un-weathered soils, P exists primarily as calcium bound phosphate (ex. apatite) (Brady and Weil, 1999). These P containing compounds have different solubility. Chemically the solubility characteristics have been used to fractionate the different PP compounds. These compounds are often categorized as being either biologically **labile** (directly available for biota uptake or recyclable via biological and chemical transformations) or **refractory** (generally unavailable for biological uptake and subject to burial). Labile forms of P decompose quickly whereas refractory forms require several months to years to become available. Table 1 shows a list of prevalent P compounds and their biological availability. Phosphate sequential extractions serve to identify these PP compounds (Castro and Torrent, 1998; James and Barko, 2005). Little is known about the dynamics and transformations of P as sediments are transported in the main channel of large rivers to receiving waters (House, 2003). This information is needed in order to better predict P fluxes through large tributary networks (Alexander et al., 2000).

Table 1. Operationally defined particulate P fractionation compounds. Labile P is directly available for uptake by the biota via eH and pH actions and equilibrium processes. Refractory has lower biological availability and is thus subject to burial (James and Larson, 2008).

Variable	Biological Availability
Loosely-Bound PP	Biologically labile; available for uptake
Iron-Bound PP	Biologically labile; available for uptake
Aluminum-bound PP	Biologically refractory; subject to burial
Calcium-bound PP	Biologically refractory; subject to burial
Labile organic PP	Biologically labile; available for uptake
Refractory organic PP	Biologically refractory; subject to burial

P Usage in biological systems

In terms of water quality, SRP is the most detrimental form because it is readily available to algae for growth (Larson et al., 2002). Biologically, P is taken up by biota for many different purposes including cell division, adenosine triphosphate(ATP), phospholipids production, etc. (Caraco, 2009). This process of going from inorganic to organic form via microbial transformation or immobilization in the aquatic system is a similar to biological processes in soils or the terrestrial system.

Phosphorus in the environment causes the most problem because of the biological interactions. Since P is an essential element for living organisms, its higher concentrations also lead to higher rates of bacterial and plant growth. An alga, for example, uses P to increase its production rate. Since P is often the main limiting nutrient in freshwater systems, its abundance instigates plant growth. An extreme increase in plant biomass then exerts more pressure on the system for continued growth. When a resource

such as oxygen, available light, or carbon dioxide becomes depleted, the excess growth dies off and starts its decay. Decomposition uses oxygen at an even high rate, and thus leads to anoxic conditions, or eutrophication (Schindler, 1977; House, 2003). Anoxic (low oxygen levels) conditions are particularly detrimental to aquatic organisms such as fish and most invertebrate species. It was these anoxic conditions in 1988 that were partially responsible for the fish kills in Lake Pepin (Randall et al., 1998; Larson et al., 2002; Heiskary and Wasley, 2011).

Environmental/Natural Sources of P

Although P has little to no gaseous forms in nature, it can be found in the snowmelt or the rainwater due to dust in the atmosphere. Rain drops are composed of particulate matter such as dust particles around which water condenses. This particulate matter may have P adsorbed onto its surface. The dust particles may have been picked up from P rich places, such as agricultural fields, and then later carried to other places in the landscape. TP concentrations as large as 0.5 mg P/L of rain have been measured in urban rainfall (Gibbs and Doerfer, 1982). In 1988 the national median TP phosphorus concentration from urban metropolitan storm runoff was 0.25 mg/L (Litke, 1999). These small P concentrations in rainfall can accumulate into substantial loads. For instance, in a North Carolina basin where rainfall averages 109 cm/year, an average P concentration of 0.06 mg/L in rainfall corresponded to a loading rate of 66 kg of P per square kilometer per year (McMahon and Woodside, 1997). This was equivalent to 22 % of the TP loading in this basin.

In an average year the Minnesota River basin has an atmospheric TP load (dry +wet) of 78, 564 kg/year (Twaroski and Reding, 2003). However, this load is highly influenced by weather patterns. For atmospheric P in a river basin or specific watershed, the variation in precipitation can have a significant effect on wet phosphorus deposition. In 2003, the atmospheric TP load (dry + wet) in the Minnesota River Basin was 78,528 kg/year. In 2007 the wet P deposition decreased by 21%, however the dry P deposition estimates were higher; with a total deposition load of 125,436 kg/year (Twaroski et al., 2007). Since dry deposition is more dependent on local site conditions and is typically surface

driven, an individual monitoring site may not be representative of the whole surrounding area. The above estimates are from one monitoring site at Lamberton, MN; which the MPCA assumed as a representative site for all SW Minnesota (Twaroski and Reding, 2003). This introduces some uncertainty in the application of these numbers to the entire Minnesota River watershed. In any case, the influences of atmospheric deposition should not be ignored.

Phosphorus Exchange between Soils and Water

Soils have the ability to adsorb or desorb P. This transformation between adsorption and desorption depends upon P concentration in the solution relative to P concentration on soil particles. The relationship between the solution phase and the adsorbed phase P concentration is called an adsorption or a desorption isotherm. The degree to which P adsorption or desorption occurs in soils depends upon charge properties of the soil, soil pH, organic matter content, mineral make-up, and reaction time. A more in-depth analysis of adsorption isotherms will be broken down later in this thesis.

There are many different mechanisms that fix P in soils. In acidic soils, there are three common mechanisms for P adsorption: First, most of the P adsorption occurs when $\text{H}_2\text{PO}_4^{-1}$ ions react with or become adsorbed to the surfaces of oxides such as $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Brady and Weil, 1998). These hydrous oxides are present on clay particles as both crystalline and non-crystalline structure and as coating on the interlayers and external surfaces. The negative dissolved anions of P may thus attach to positive charges of the oxides by electrostatic forces. However, depending on time the attraction may weaken and the P at the surface may be knocked off from the positively charged sites by other anions, such as OH^- , SO_4^{-2} or organic acids. Thus this P is readily available for use since it is only located at the particle surface. To increase the release of adsorbed P from soil particles producers sometimes add organic matter (OM) which releases organic acids capable of replacing $\text{H}_2\text{PO}_4^{-1}$ more quickly (Barrow, 1983; Brady and Weil, 1998). Over time the P may penetrate the mineral structure and thus become more difficult to remove or may require extra time for removal. This net process of initial adsorption followed by penetration is called sorption. When the adsorbed P penetrates into the soil

particle it also reopens adsorption site on the soil particle surface to create a two-step adsorption process (Brady and Weil, 1998; Barrow, 1983, Sparks, 2003).

The second mechanism for P adsorption in acidic soils is chemical integration of P with the oxide surface. This mostly takes place on clay particles and results in a binding that is sufficiently stronger and is able to withstand being replaced by other anions. P bound through this mechanism has very low solubility or low desorption potential which results in low availability of P for plant growth.

A third mechanism for P adsorption on acid soils occurs over time when P becomes buried inside the oxide particle as more iron and aluminum hydrous oxides precipitate and cover the bound P (Brady and Weil, 1998). This mechanism is also the most permanent. Only extreme environmental changes, such as the removal of the overlying precipitated oxides would release this bound P.

In alkaline soils (soils with a pH=8), the dissolved PO_4 reacts with Ca to form a sequence of products. As the time and the sequence continue the products become increasingly unavailable and P can become permanently bound. Calcium bound P is often described as refractory due to this rapid sequence of transformation (Brady and Weil, 1998; James et al., 2002). Labile forms of inorganic P dissolve quickly while refractory forms require several months to a year to degrade (Larson et al., 2002). The above binding process is similar to the second adsorption process explained for acidic soils; in that the phosphate ions bind with the calcium carbonate in soil and becomes chemically integrated. P availability in alkaline soils is determined by the solubility of calcium bound P compounds.

Besides adsorption, inorganic phosphorous in soil solution may also be converted to organic P through microbial transformations. Similarly, organic phosphorus may also mineralize to inorganic phosphorus via the decomposition processes (Larson et al., 2002; Holliday and Gartner, 2007). Figure 7 shows the linkages between various forms of P throughout the P transformation cycle.

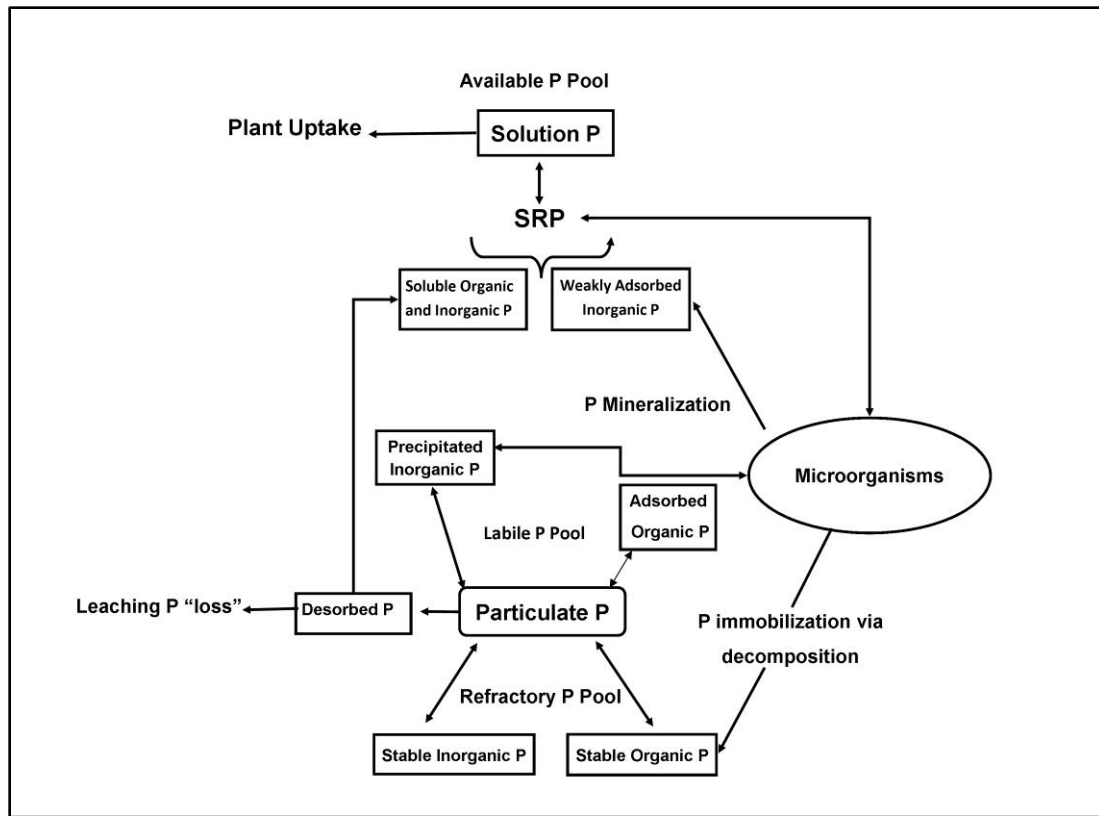


Figure 7. Linkages between various forms of P via transformation cycles (after Holliday and Gartner, 2007).

Phosphorus Cycling in Aquatic Systems/Lake Pepin

Phosphorus is highly cyclic in that it can be consumed and recycled rapidly within an aquatic system. Also, it has many fates depending on abiotic and biotic factors affecting the aquatic system. In a general aquatic system P has three destinies: (1) It may be taken up by bacteria, fungi, grazers or phytoplankton primarily as SRP. It can stay in this form indefinitely, as the phytoplankton decompose and re-release it as SRP. (2) It may exist in buried sediments. Much of the P in buried sediments is from sinking soil particles with adsorbed P, or from decomposing organic matter such as plants or phytoplankton. (3) It may be transported downstream or out of the system (Caraco, 2009).

Soil particles can easily adsorb P onto the particle surface (destiny #2) but the P buffering capacity of a soil-water system depends on both biochemical and physical processes. If a lake bottom lacks oxygen, the soil particles will be more chemically inclined to release

the adsorbed P. This released P is referred to as desorbed P. The desorbed P is then in a dissolved form such as SRP and can again be used to fuel plant growth as described under destiny #1 or it may be transported out of the aquatic system (destiny # 3). All three of these destinies intertwined, thus there is not one ultimate and final fate for all P (Wetzel, 2001).

Another aspect of this thesis research deals with the presence of P in Lake Pepin sediments. When P exists in buried sediments, these sediments can act as either a sink or source of P within the water column. Based on sediment cores taken from Lake Pepin, Engstrom et al. (2009) reported relatively uniform TP concentrations varying from 600-800 mg/kg in pre-settlement times (prior to 1850) to as high as 1600-1800 mg/kg in the period 1950-1970 with a smaller peak of 1000-1400 mg/kg in the period 1890-1910. Starting in 1970, there has been some decline in TP sediment concentration especially in upper and mid lake cores (transects I-III) with current concentration of TP varying from about 800 mg/kg in the upper end of the lake to 1500 mg/kg in the lower end of the lake. This is likely due to efforts in controlling point source P inputs to the upstream rivers. Engstrom et al. (2009) also suggested that recent lower TP concentration in Lake Pepin sediments could be due to increases in calcium carbonate concentrations and/or due to dilution from sediments with limited P holding capacity. Overall a 15 times increases in P accumulations rates were reported for the last 200 years (Engstrom et al., 2009).

Based on diatom population, Engstrom et al. (2009) further inferred TP concentrations in Lake Pepin waters and suggested that the increase in TP starting around 1860 was due to the European settlement and land clearing in the area whereas the increase around the turn of the century was due to an increase in nutrient loading.

Although sediment core analysis has shown that P concentration have increased in Lake Pepin since the settlement times (Engstrom et al., 2009), it is not clear how and to what extent the natural stream banks erosion may have contributed to this increase in TP in Lake Pepin. One suggested viewpoint is that the landscape conversion to agricultural crops and practices of draining wetlands are the primary reasons why P and

sedimentation have increased in Lake Pepin in recent years (Engstrom et al., 2009). Using magnetic susceptibility and pollen data, Engstrom et al. (2009), has suggested that acceleration of surface runoff and soil erosion began almost immediately after prairie and forests were replaced by cropland. This will suggest that anthropogenic activities are the main cause for increased sedimentation rates in Lake Pepin. However analysis of alluvial stratigraphic record also shows that the rates of erosion and sediment deposition in Lake Pepin are complex with many variables and somewhat different interpretations. For example, based on bathymetric data and Cs-137 concentration in sediment cores, McHenry et al. (1980) showed that sedimentation rates since 1954 were slightly greater than 2.5 cm per year in the upper part of the Lake Pepin but these rates were somewhat less than those from previous half century (1895-1954). Using bathymetric data, Maurer et al. (1995) reported that lake volume decreased by 21% between 1897 and 1986 but most of this volume decrease occurred in the upper part of the lake, being influenced by the moving delta at the head of Lake Pepin. Engstrom et al. (2009) explained the differences between different studies based on the possibility of inaccuracies in bathymetric data. However, one should be careful in giving more weight to data from 10 cores as in Engstrom et al. (2009) study compared to the full scan of the lake bottom in McHenry et al. (1980) and Mauer et al. (1980) studies.

In addition to the above differences in characterization techniques, there are also possibilities of complications in Lake Pepin sediment stratigraphy from historical events/activities. The Lake Pepin TP declines in 1920 were suggested likely from temporary interruption of watershed disturbance and reduced flow during the 1930s due to the dust-bowl period (Engstrom et al. 2009). Moving forward chronologically, the increased TP concentrations of lake waters starting in 1965 was suggested due to pollution from industrial activities. Most recently the diatom inferred analysis shows a continuous increase in TP concentration of the lake waters from 1975 to present; however, there is no suggested historical explanation for this increase (Engstrom et al., 2009).

The type of P bound to the sediment is an influential factor considering whether the PP is labile or refractory. James and Barko (2005) showed how material may have different fractional compounds adsorbed onto the particle phase. For Lake Pepin sediments, Engstrom and Almendinger (2000) reported NaOH extract or iron/aluminum bound P as the dominate fraction (Fig. 8 Purple line). It is also interesting that this one fraction is driving the increases in sediment TP concentrations since 1850. This is based on the observation that the Ca P (difference between green line and purple line) and organic P (difference between red line and green line) concentrations (mg/kg) are nearly constant over time) and hence most of the increase in TP is due to an increases in NaOH extract P (iron/aluminum P; Purple Line). The continuous increase in NaOH extract P over time with some decrease starting around 1970 would suggest adsorption dominated processes controlling P in Lake Pepin sediments. While the authors would concentrate on inorganic P comparisons (iron/aluminum plus calcium-P; green line in Fig. 8) in this thesis, TP concentrations are the preferred P form for reporting by regulatory agencies and we will report those values regularly throughout this thesis.

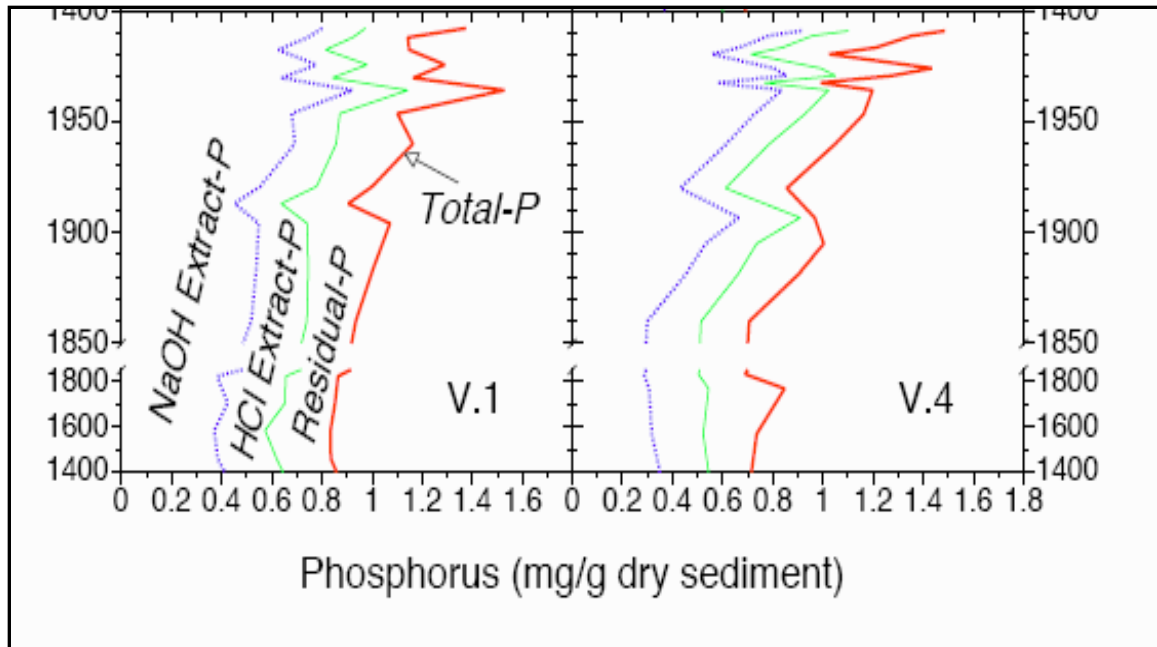


Figure 8. Plot of sequentially extracted P concentration vs. depth in Lake Pepin sediments. Purple line represents iron/aluminum P, green line represents sum of iron/aluminum P plus calcium P (inorganic P), and the red line represents the sum of iron/aluminum P, calcium P and the organic P (total P). The difference between green line and purple line represents Ca P. Similarly the difference between red line and green line represents residual or organic P (Engstrom and Almendinger, 2000).

Physical and Chemical Controls Influencing P in Aquatic System

For a given aquatic system (lake or river) different forms of P may predominate. The dominance of a given P form depends on both physical and chemical properties of the aquatic system. The following text outlines the most influential parameters in each of these categories and how they may affect the P levels in a given water systems.

The physical parameters that are most pertinent for P dynamics in aquatic system are geology, hydrologic properties such as lake turn over, stream flow rates, residence time, and temperature, and whether the system is open/closed (Coelho, 2004). The geology of the stream and surrounding environment determine the mineralogy and geochemistry of the local stream sediments. For example, stream systems where the weathered bedrock is rich in iron and aluminum hydroxides are expected to generate sediment with high

adsorption capacity (Withers and Jarvie, 2008). Comparatively, if the system has an apatite base then the P is likely associated with the calcareous mineral and will be less bioavailable than P bound to iron and aluminum hydroxides (Sharpley et al., 1992). The local geology also influences sediments' chemical and physical characteristics, such as particle size distribution, organic matter content, and forms of water extractable P (Haggard et al., 2007).

Within a mixed-land use watershed, flow type (i.e., base flow vs. storm flow) has been found to be an important factor controlling P losses. For example a watershed dominated by storm flow could contribute as much as 80% of the annual TP loss to the river system during the storm events; with the remaining 20% of the annual TP load found in base flow. This divergence is because the volume of runoff generated increases as the storm size increases and increased overland flow means more energy to erode soil particles that are rich in TP. As such there is a direct relationship between the amounts of TP being exported from a watershed as a function of the storm size; larger storms exporting/moving larger amounts of soil and thus TP (Sharpley et al., 2008). Thus a 100 year storm event can have extremely detrimental effects on the environment both in terms of sediment and nutrient export. An example will be the massive mud slides that Lake Superior experienced during the summer of 2012 due to an extreme rainfall event (one in 500 year event) (Kraker, 2012).

The type of flow also determines the type of P export. For example, Sharpley et al. (2008) reported that in an upland agricultural watershed dominated by surface or near-surface flow, base flow was generally comprised of 79% PP (21% SRP) compared to 54% (46% SRP) in storm flow. However, the storm flow still carried much larger TP losses (76%) than the base flow (24%) on an annual basis thus suggesting that the storm flow was the more important driver for P transport. An interesting aspect of this watershed is that while the high intensity rain events (> 10 year event) exported large quantities of P (21%), it was the more frequent low intensity storms (< 1 year event) that carried more P during the 10 years of monitoring (Sharpley et al., 2008). The implication

of this research is that for this type of watersheds, BMPs designs should be for lower intensity events.

A physical influence of flow type is its effect on residence time of sediments which in turn controls the P availability for biota. Desorption processes are sensitive to the contact time; shorter contact times between soil and water producing an initial quick soluble P desorption but no re-adsorption. Comparatively, longer exposure time may result in the re-adsorption of P ions (Barrow, 1979). One possible reason for 54% PP and 46% SRP in Sharpley et al. (2008) study may be the shorter residence time that encouraged rapid P desorption from sediments.

Another physical parameter which has a strong influence on P concentrations in the aquatic system is the temperature. Increased temperature acts as an endothermic catalyst and increases the rate of reaction for both adsorption and desorption processes. Thus when dissolved P concentrations are low or when physical conditions are tipped towards desorption, temperature has been shown to increase P solution concentration from increased sediment P desorption. Similarly, higher temperatures can also accelerate the conversion of P from the dissolved to the particulate form. Barrow (1979) found that the rate of adsorption at 62°C was about 40 times faster than at 25 °C. However, there is no physical evidence which suggests higher temperatures also lead to greater quantities of P adsorbed/desorbed; they simply increased the rate of reaction.

Chemical properties which have an influence on P flux are: pH and oxygen levels in relation to redox potential (Coelho, 2004). Within soils, it has already been shown that pH affects the ionic species of P. However, within aquatic systems pH may also influence the adsorption processes. Barrow (1983) showed that the adsorption of P decreases as pH increases. However, these effects are not enormous, except under extremely high pH conditions; which is not the case in natural systems (Barrow, 1983).

Another important chemical factor controlling P concentration in aquatic system is the oxygen concentration. Oxygen plays an important role in the availability of P through the

formation and interactions of iron bound P compounds. It is for these reasons, iron bound P in lake sediments are a significant factor in continued lake eutrophication and are a focal point of water quality research in freshwater ecosystems (Coelho et al., 2004; Caraco, 2009). Under aerobic conditions such as in a normal water column, when iron and P bind together due to surface charge, the iron is in its insoluble Ferric (III) state and thus the P compound precipitates out. However if the dissolved oxygen levels drop in the water column or if the compounds sink and become buried in the sediment where there is reduced oxygen levels, then the reducing environment makes it possible for the reduction of iron compounds from Fe^{+3} to Fe^{+2} , or from ferric (III) iron to ferrous (II) iron. Ferrous (II) iron compounds are more susceptible to labile processes; meaning the compounds are more likely to return from the precipitated state to a dissolved state and become re-suspended in the water column. At the same time, when the Fe^{+3} is reduced to Fe^{+2} the surface charge attached P is also released into the water column. This released P can act as a continuous source of P over time and may be reused and recycled (Brady and Weil, 1998).

Since legacy sediment can release bound P, eutrophication may persist for years even if upstream sources of sediment bound P are removed, or reduced. Hence aquatic chemists are concerned with both P released by legacy sediments as well as the incoming sediment bound P (James et al., 1996; Brady and Weil, 1998). To assess the potential internal recycling of P in lakes, legacy sediments are exposed to anaerobic conditions in order to find their maximum desorption potential. Based on 20 Minnesota lake sediments, Bischoff (2011) showed that anoxic P release varied from 0 to 30 mg/m^2 per day. Comparatively, P release under oxic (>2 mg dissolved oxygen) varied from 0 to 0.8 mg/m per day. Results of these studies suggest that internal sediment phosphorus release is an important process in most Minnesota lakes and should be quantified as a part of any diagnostic study. In addition to the high anoxic P release rate, recent research has also shown that these release rates vary as a function of lake depth. James (2011) reported the P release rates of $> 10 mg/m^2$ per day occurring at depths > 7.5 meters (max depth = 11.5 meters).

Adsorption Isotherm

Types and Interpretation

As outlined above, a variety of physical and chemical factors influence how P is found in the aquatic environment. The major source of P in the aquatic system is the sediment bound PP. Phosphorus concentrations in sediments in turn are controlled by dissolved P concentrations of river or lake waters. Adsorption and desorption processes determine the relationship between sediment P and solution P concentrations and these relationships are called adsorption or desorption isotherms (Froelich, 1988). The ability of a soil/sediment to adsorb or fix P into unavailable or insoluble forms is called the P fixation capacity (Brady and Weil, 1998). It could also be viewed as the total number of sites on soil particle surfaces capable of reacting with P ions.

There are three main types of adsorption isotherms: linear, Freundlich, and Langmuir (Fig. 9). A linear adsorption isotherm is a straight line relationship between the sediment adsorbed P and the solution P concentrations. In other words, there is a constant rate of P adsorption irrespective of the solution P concentration. Comparatively, the Freundlich adsorption isotherm displays a slower rate of P adsorption with an increase in solution P concentration. This trend is most apparent when large ranges of P solution concentrations are utilized compared to the linear isotherm (Jury and Horton, 2004). Langmuir adsorption isotherm is a more generalized form of isotherm and encompasses both linear and Freundlich adsorption isotherms. The unique feature of the Langmuir adsorption isotherm is that it displays a finite capacity for adsorption above a certain P solution concentration (Fig. 9). The initial linear region of P adsorption in Langmuir adsorption isotherm is similar to the linear adsorption isotherm and is thought to be controlled by the surface charge on the oxides and clays (Castro, 1998). When the Langmuir isotherm approaches a zero rate of adsorption, this indicates the soils have reached the maximum capacity for P fixation (Jury and Horton, 2004).

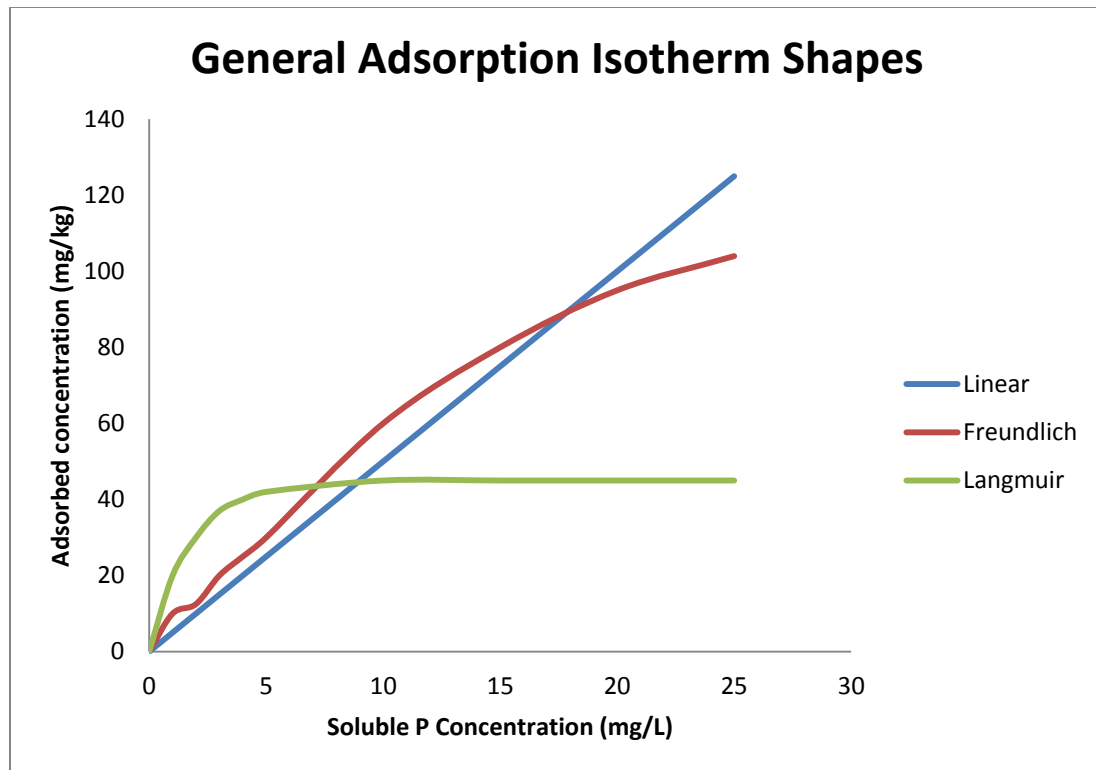


Figure 9. Shapes of three different P adsorption isotherms (after Jury and Horton, 2004).

In addition to the three basic isotherms mentioned above, adsorption has also been described in many other ways. The three adsorption mentioned above are thought of as equilibrium based adsorption models. However, Sposito (1984) categorized adsorption isotherms into four general categories naming them S (S-shaped slope), L (Langmuir), H (high-affinity), and C curves. Additional adsorption models include the Gouy-Chapman model which utilizes a double layer theory. This theory describes the sorption behavior as ionic distribution in a diffuse layer formed adjacent to a charged surface. The surface complexation model builds on the double layer theory and considers the proton dissection, metal cation and anion adsorption, and multiple competitive adsorption reactions on oxides (Sparks, 2003). In addition to these adsorption models, there are an infinite number of specialized models. However, a review by Westall and Hohl (1980) found that each specific model had one major problem in that the models are developed and employed to fit the experimental data. Thus Westall and Hohl (1980) believe that one model is as good as another in describing material balance data. However, the conflict

arises when these models are applied to data other than the experimental data. Therefore, more generalized adsorption models are more appropriate; hence this authors' rational for using the equilibrium based adsorption models.

Several factors influence the characterization of individual adsorption/desorption isotherms. These factors include the soil: water ratio, exposure time and the range of dissolved P concentrations. Arbelaez (2003) used a 1:25 soil: water ratio to describe P sorption to stream sediment. These authors used the Langmuir model to describe their adsorption data. Exposure time between sediment and solution is also important in adsorption isotherms because in some cases prolonged exposures can lead to saturation of all available P adsorption sites (Malueg et al., 1975). Haggard (2007) observed a two phase sorption process where the P ions over time penetrated the particle thus making the surface locations open for re-adsorption. Finally range of dissolved P concentrations is also a strong experimental factor. Latterell et al. (1971) used a range of P concentrations from 0.05-42 ppm in their equilibrium studies involving lake sediment. The isotherm patterns in this study were closer to linear and Freundlich isotherms than the Langmuir isotherm due to the range of P values used in this study.

One should also be careful in the interpretation of isotherms in that they are descriptions of macroscopic processes and do not suggest any given reaction mechanism. For example, some researchers have used the Langmuir isotherms to suggest that the flat slope observed at higher concentrations represents precipitation. This would be an incorrect interpretation as precipitation and adsorption can occur simultaneously (Sparks, 2003).

Interpretation of the Adsorption Isotherm (Slope and EPC_0)

Depending upon the type of adsorption isotherm there could be various interpretation of the behavior of sediments to P sorption/desorption. One of the variables is the slope of the isotherm. The slope reflects the intensity of P binding to soil particles. The steeper the slope, the greater is the binding ability. The x-intercept refers to the equilibrium P concentration in solution when there is zero adsorption (EPC_0). The EPC_0 of sediment is often used to evaluate whether the sediments will act as a P source or sink in the flowing

waters (Froelich, 1988). When stream sediments have a low EPC_0 value, sediments will adsorb/sequester P from the water column, thereby reducing the P concentration in the stream water. However, if the sediments have a higher EPC_0 value than the water, the sediments will act as a source of P. Depending upon the level of sediment P concentration in relation to the water concentration, desorbed P could be a major nutrient source for algal growth, especially during low flow periods.

Ideally the sediment EPC_0 should be roughly equal to the stream P concentration; an equilibrium condition between the sediment and the water column P (James and Larson, 2008).

Several studies have found a strong positive relationship between sediment EPC_0 and the stream water SRP concentrations (Arbelaez, 2003; McDowell et al., 2003, James and Larson, 2008). This suggests that either the stream sediments have a major control on the SRP concentrations of the river water or the EPC_0 of the sediment changes rapidly in response to SRP of the river water. Research has also been reported where the SRP in river water was not the same as EPC_0 , thus suggesting that EPC_0 is not a major controlling factor of P concentration in the water column and the EPC_0 of the sediment does not change when in contact with river water. Arbelaez (2003) found that although the physical and chemical characteristics of her river channel remained constant, the EPC_0 of sediments at the third location was much higher. At this site animals had access to the stream. Arbelaez (2003) could not conclusively state that the animal access caused the increase in EPC_0 ; especially since water samples were never taken when animals were accessing the stream. The author theorized the animal interaction with river water was likely the main contributor. In these types of environments, the sediments are not rendering control over stream SRP values, but are being influenced by outside factors. These factors include high discharge sites or anthropogenic influences that cause an artificial increase in sediment P concentrations at a localized scale (Haggard et al., 1999; Arbelaez, 2003).

The EPC_0 may also be related to physical properties such as particle sizes or location of sediment origin. Haggard et al. (1999) found that EPC_0 was significantly correlated with

% silts in the sediment. Just like soils with different land uses, sediments from different sources may have different EPC₀ values. Overall river sediment as a group could be acting both as a source and scavenger of P in the river water column.

Some EPC₀ characterization of river sediments for locations both upstream and downstream of our study site as well as at locations outside Minnesota has been reported in the literature (Table 2). For example, James et al. (2002) showed that EPC₀ of river sediments in Redwood River (situated on the Minnesota River upstream of the Blue Earth/Minnesota River confluence) was 0.074 mg/L. Comparatively, EPC₀ of the river sediments in the Minnesota River before the confluence with the Mississippi River (from river miles 39.4-3.5), downstream of our study site was 0.117 mg/L (James and Larson, 2008). Further downstream, James and Barko (2004) reported the EPC₀ value of 0.155 mg/L for surface sediments in Lake Pepin. However, all these values are much lower than the EPC₀ values (mean=0.34 mg/L; range=0.062-0.69 mg/L) of surface agricultural soils in the Minnesota River Basin reported by Fang et al. (2002). The increasing trend in EPC₀ values from the Minnesota River Basin towards Lake Pepin suggests that river sediments are likely scavenging P from the river water column as they are tumbling downstream to Lake Pepin.

Table 2. EPC₀ values of river sediments and surface agricultural soils in the literature.

Location	EPC₀ Point (mg/L)	Reference
Redwood River Suspended Solids	0.074	James et al. (2002)
Minnesota River Suspended Solids	0.117	James and Larson (2008)
Lake Pepin Sediment	0.155	James and Barko (2004).
Minnesota River Basin Agricultural Soil	0.34	Fang et al. (2002)
Eau Galle River	0.129	James and Barko (2005)
Colorado River	0.040	Mayer and Gloss (1980)
Bermejo River (Argentina)	0.060	Carignan and Vaithyanathan (1999)
Bear Brook	0.002	Meyer (1979)
NY wooded streams	<0.002	Klotz (1985)

Lower Mississippi River	0.108	Wauchope and McDowell (1984)
Xiangxi River (China)	0.100	Chang-Ying et al. (2006)

Sediment Enrichment during River Transport

Till now we have presented the adsorption characteristics of sediments under static water conditions at a given location. However, there are interactions between the physical and chemical properties affecting P adsorption and the sediment transport processes in a river system. One of the most important changes is that coarser fractions remain behind and finer fractions move downstream, a process called particle sorting or particle enrichment. The other important change is P adsorption or desorption depending upon the river water concentration. James (2010) conducted preliminary research to answer some of these questions. His research involved (1) quantifying various P pools as a function of river sediment particle size distribution, and (2) assessing the EPC_0 of various particle fractions. The underlying hypothesis was that finer grained materials have a larger capacity to sequester P than the coarser grain particles. Several studies have shown that TP concentration increases with a decrease in particle size (Day et al., 1987; Agbenin and Tiessen, 1995; Sinaj et al., 1997). This is due to greater surface area per unit volume of finer particles (silt and clay) and thus higher concentration of iron and aluminum compounds that are sorption sites for P.

In addition to higher adsorption in finer particles, there is also a shift in EPC_0 values with a decrease in particle size. Schematically, Fig. 10 shows the lowering of EPC_0 values with an increase in particle size (James, 2010). The slopes of the lines represent the binding ability whereas their intersection with the x-axis depicts zero net P adsorption or desorption point (EPC_0). In this study, James (2010) characterized the P adsorption characteristics (EPC_0 and the slope of the adsorption isotherms, K_d) for various size fractions in the Minnesota River sediments 10 miles upstream of the Minnesota/Mississippi confluence. As expected, results showed a distinct increasing trend in (1) TP content, and (2) binding ability (K_d values) with a decrease in particle size. There was also some increase in EPC_0 values with decrease in particle size but the

trend was not definitive. James (2010) reported a 4:1 ratio in TP concentration for clay (<3.95 μm) compared to the sand (>63 μm) particles (Table 3). K_d values varied from near zero for sand fraction (<63 μm) to around 425 L/kg for clay (<3.95 μm) size particles.

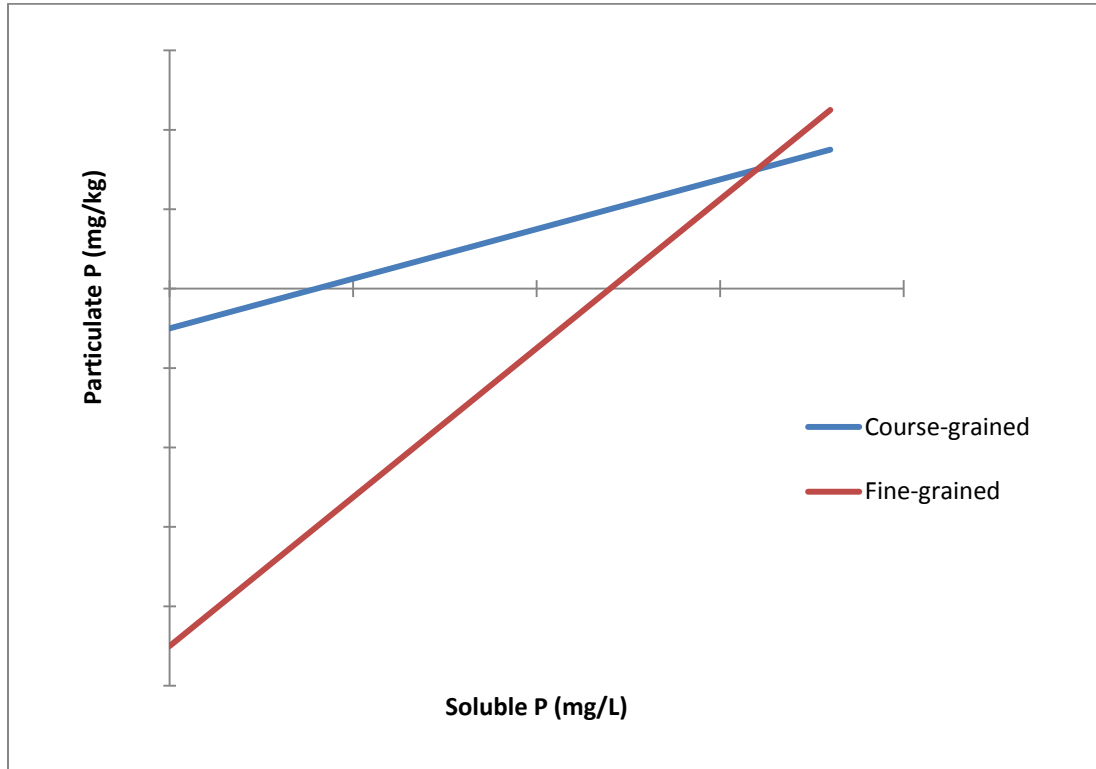


Figure 10. Hypothetical relationships between the particulate P and soluble P for two different size particles (after James, 2010). The slopes of the lines are the partitioning coefficients (K_d values) and intercepts with x-axis are the EPC_0 values.

Table 3. Total P (TP) concentrations and their relative ratios for various size fractions in the Minnesota River sediments (James, 2010).

Particle Diameter (μm)	TP (mg/kg)	Relative Ratios
>63	265.5	1.0
31.2-63.0	398.3	1.5
15.6-31.2	512.1	1.9
7.8-15.6	531.0	2.0
3.9-7.8	796.6	3.0
<3.95	1100	4.1

Further sequential fractionation of PP in the Minnesota River sediments (Fig. 11) showed that concentrations of TP, loosely bound P, iron bound-P, aluminum bound-P, and organic P increased with decreasing particle size diameter but the refractory calcium bound-P concentrations remained constant over the range of particle sizes (James, 2010).

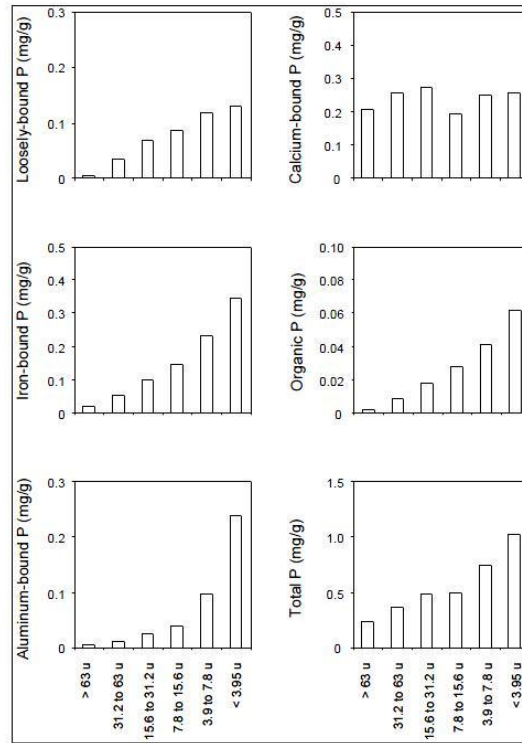


Figure 11. Variations in loosely bound P, iron-bound P, aluminum-bound P, calcium-bound P, organic P and total P as a function of particle size diameter in the Minnesota River sediments (James, 2010).

James (2010) results are similar to the results from other studies reported in the literature on relationship between particle size and quantity/ type of P. Day et al. (1987) reported that TP content in soils is directly associated with the amount of clay. Hanley and Murphy (1970) reported that in general, all forms of P are highest in clay particles versus sand particles. They also found that for clay and silt fractions, inorganic P was mainly iron bound P. Comparatively, calcium bound P was the dominant form in the sand fraction. More recently Owens and Walling (2002) reported different PP concentrations associated with different portions of river sediment, such as floodplain, channel bed

sediment, and suspended sediments. These authors believe that this primarily reflected the differences in the particle size composition between different types of sediments.

Historical Sources of P Contribution to Minnesota Rivers

In order to explain P accumulation in Lake Pepin sediments, it is important to identify possible P sources contributing to various rivers in Minnesota. These sources have changed over time from non-point source in pre-European settlement, to point and non-point sources in post settlement time. Traditionally rivers were viewed as having the capacity to rejuvenate themselves, and thus early settlers used the rivers as conduits for removing waste from cities. With the realization that some of the waste was staying in the rivers and choking the river ecosystem, efforts were made to control this pollution from point sources. The following text briefly describes the evolution in the usages of various rivers in Minnesota.

Minnesota was recognized as a USA territory in 1849 and officially became the 32nd state on May 11, 1858. Total population varied from 6,077 in 1850 to 172,023 by 1860 (Dole and Wesbrook, 1907). By the late 1880s Minneapolis and St. Paul were each dumping about 500 tons of garbage each day into the Mississippi River (Scarpino, 1985). The quantity of garbage grew to such a large level that in 1888 the Army Corps of Engineers, charged with maintaining the river navigation, removed a bar on the Mississippi River composed of decaying garbage. In 1910, Harriet island beach in St. Paul was closed due to excessive bacterial count from the sewage and garbage dumped upstream (Marks, 2010). This anthropogenic created garbage contained P; however the exact quantity is not available in historical records.

In addition to the domestic and or/industrial garbage, another highly significant source of P to the Upper Mississippi River system, was likely the animal waste from South St. Paul Stockyard. Opened from 1886 -2008 the original owner, Stickney, specifically choose the stockyard location because of its proximity to the railroad and to the Mississippi River (Anfinson, 2003). Dole and Wesbrook (1907) described the effect of South St. Paul Stockyard on the water quality of the Mississippi River as “*On the Mississippi River, just*

below St. Paul; water for the public supply is furnished from private artesian wells at Swift & Co.'s packing house. Ice supply for storage is cut from small lakes in the vicinity. No sewerage. Garbage is hauled from the stockyards and dumped near the river.” In 1900 the meat packing industry was Minnesota’s 4th largest industry (Anfinson, 2003). Table 4 lists an approximate numbers of animals that were processed or passed through this one stockyard.

Table 4. Reported number of animals which were processed or passed through the South St. Paul Stockyard (http://en.wikipedia.org/wiki/South_St._Paul,_Minnesota#The_Kaposia).

Livestock	1888	1896
Cattle	31,514	92,062
Calves	2,212	200,413
Hogs	272,710	/
Sheep	61,343	200,413
Horses	806	/
Total	368,585	~492,888

According to the above report, over 360,000 animals were moved through this one stockyard in 1888 and the operation of this stockyard only grew in size over time. In earlier years, all of the animal manure and waste from the processing was disposed of in the Mississippi River; a main reason why the original owner Stickney chose this site. Figures 12-14 show historical photos from the South St. Paul stockyards daily operations. Although many improvements were likely made over time in the stockyard in terms of waste disposal, the stockyard only closed recently in 2008.



Figure 12. Sheep moving through the stockyard (Courtesy of Dakota County Historical Society).



Figure 13. Cattle pen at South St. Paul Stockyards in 1930(Courtesy of Minnesota Historical Society).



Figure 14. Union Stockyards in South St. Paul, including pens, and alleys (Courtesy of Dakota County Historical Society).

Historically, the other known point sources of P pollution to the Minnesota River and the Upper Mississippi River were the sewage treatment plants (STP), and many industrial/manufacturing facilities. Since traditionally STP only removed solid waste, these facilities were often built on/near a river to discharge waste water. Their historical impacts have only been documented since the 1930s when the first treatment plant was built in St. Paul. Even in this documentation, there is limited information on P pollution because earlier efforts of STP were mainly geared towards controlling bacterial pollution and solids (organic material which increased biological oxygen demand in rivers) (Crohurst, 1932). The earliest local record, seen by the authors, where there is any analysis on P released into river water was a Federal Water Pollution Control Administration (FWPCA) report in 1966. The report listed the TP concentrations of the effluent from sewage treatment plants along the Mississippi River between the City of Anoka and the City of Pepin and is displayed in Fig. 15. Additionally, management for P is a relatively new priority such that prior to the separation of storm water in late 1980s, the sewage treatment plants discharged raw sewage when the storm water, due to heavy rain events, overwhelmed the STP's capacity (Dr. Kuldip Kumar, 2012. Metropolitan Water Reclamation Center of Greater Chicago. Personal communication)

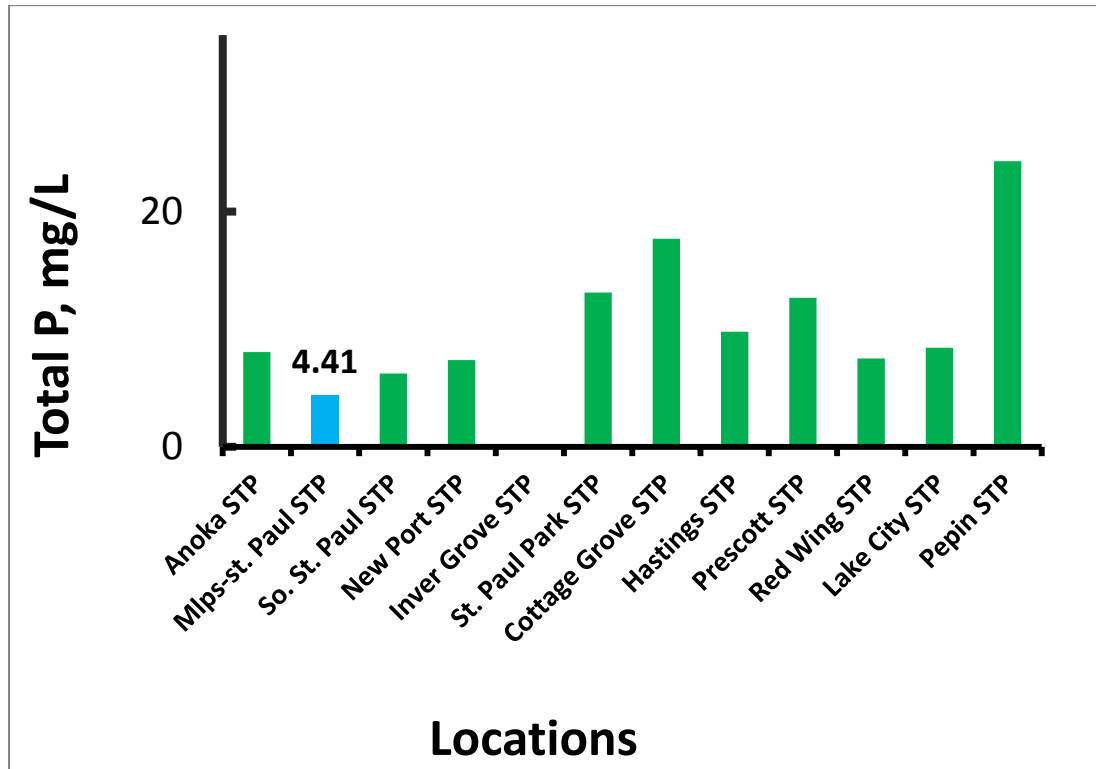


Figure 15. Total P concentrations in effluent from various Sewage Treatment Plants (STP) along the Mississippi river in 1966 (FWPCA, 1966).

The TP concentration in effluent varied from 4.41 mg/L at Minneapolis-St. Paul STP (sometimes called the Pigs Eye Plant) to 24.28 mg/L at the Pepin STP. The Pigs Eye Plant released around 189 million gallons of effluent per day with a TP concentrations ranging from 1.2-7.3 mg/L. This was equivalent to a TP load of 1123 tonnes P per year; a much higher quantity than from any other plant in the survey area. Annually the TP load from all STP, between Blue Earth and Lake Pepin, was 1375 tonnes per year.

Comparatively, the industrial sources contributed 495 tonnes of P per year between Blue Earth and Lake Pepin STP. Some of the industries contributing P to the Mississippi River upstream of Lake Pepin were 3M, NW Refining Co, NW Coop Mills, Foot Tanning Co., Blue Cross Rendering Co., Green Giant, MN Valley Milk Processing, American Crystal, Cargill, and Anderson Window. The highest TP concentration recorded in 1966 was 2946 mg/L from NW Coop Mills Ponds leakage. In comparison 3M had a TP concentration of 14.6 mg/L (FWPCA, 1966). Food industry often used dilute phosphoric acid both for

cleaning their equipment as well as a preservative in the canning process. This practice is still currently being used, although high P wastewater is not directly discharged in rivers (Dr. Kuldip Kumar, 2012. Metropolitan Water Reclamation Center of Greater Chicago. Personal communication). For example, soda producers, such as Coke, currently use phosphoric acid in sodas for cleaning and preservative purposes.

Although the earliest reporting of P input to river systems in Minnesota is recorded in 1966, we do know through sediment records that P inputs to the environment increased dramatically after the 1950s with the usage of phosphate fertilizer in both rural and urban areas, land application of sewage waste and manure, and prevalent use of new detergents. Although created in the 1940s, a peak in point source loads in 1967 reflects the increased use of phosphate-based detergents (Litke, 1999). Prior to WWII traditional bar soap was the primary cleaning agent. Bar soap contains little phosphate. However, after WWII new cleaning agents began to appear in the market. One of the key reasons was the need for more effective cleaning agent in the household washing machines. These new washing detergent contained as much as 60% by weight sodium tripolyphosphate (STPP), which is about 15% by weight phosphorus. STPP was used as a builder to remove the hardness of water so that the detergents could perform most effectively. With the increased demand for washing machines, the consumption of manufacturing detergents became significant. In 1967 these synthetic detergents were contributing 220,000 metric tons P annually to the wastewater system throughout the nation. Shortly after environmental concerns arose, the US Congress established the Joint-Industry-Government Task Force on Eutrophication. In 1970 the detergent industry voluntarily agreed to limit phosphorus in detergents to 8.7% by weight. In late 1970s additional restrictions were established on P use in detergent in many states (Litke, 1999). For Minnesota, P in detergent was limited to 0.5% by weight starting in 1977. In Wisconsin, these same restrictions were imposed in 1979 but the ban was lifted in 1982 and then reimposed in 1984. As of 1 July 2010, sixteen states now adhere to the 0.5% by weight P detergent ban including Illinois, Indiana, Maryland, Massachusetts, Michigan, Minnesota, Montana, New Hampshire, Ohio, Oregon, Pennsylvania, Utah, Vermont, Virginia, Washington and Wisconsin (Koch, 2010).

Amendments to the 1948 Federal Water Pollution Control Act, the 1972 Clean Water Act, and the 1974 Safe Drinking Water Act resulted in further reductions in point source P loads as more STP facilities adopted secondary and sometimes tertiary treatment technology (ex. Bayport and Stillwater) (Larson and Johnson, 2002). However, this level of treatment is not routinely present in the sewage treatment plants belonging to smaller communities in the study area. For instance Fig. 16 shows the average P concentrations in STP effluent in the Minnesota River Basin from 2000-2003. Half of the STP plants have SRP concentrations more than 2.5 mg/L. The Litchfield STP plant recorded the highest P concentrations of 10.8 mg/L of effluent (MPCA, 2011).

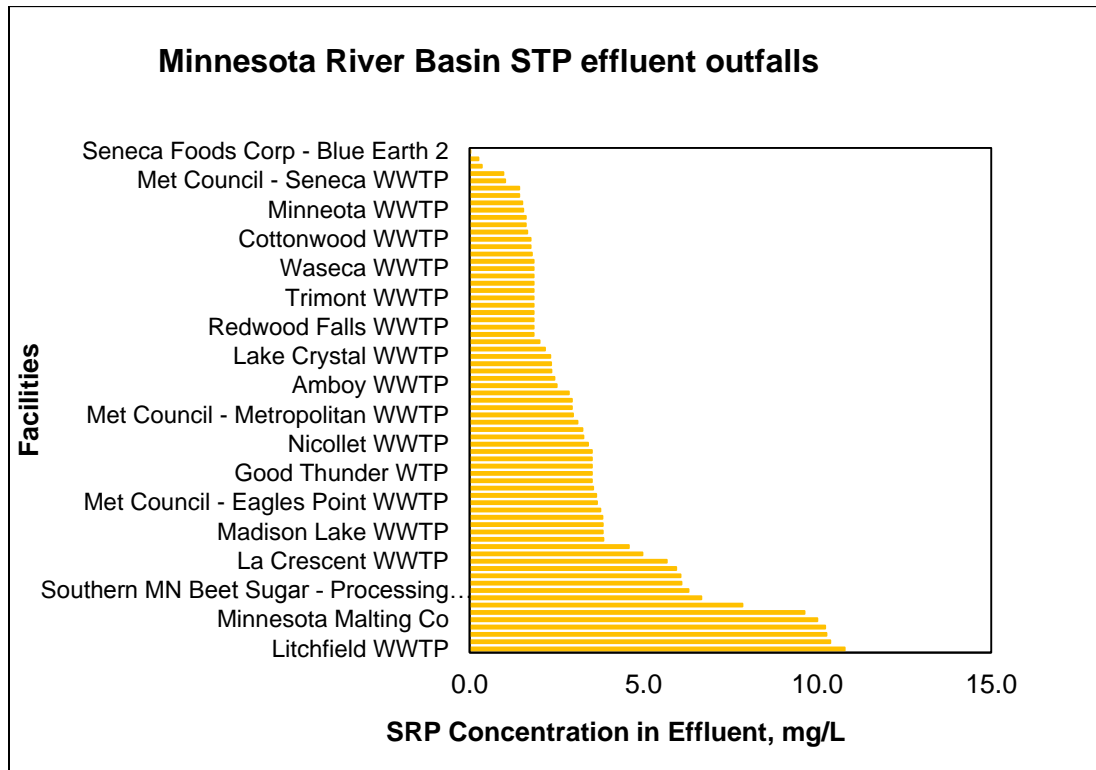


Figure 16. MPCA recorded soluble reactive P (SRP) concentrations from sewage treatment plant (STP) effluent in the Minnesota River basin from 2000-2003 (MPCA, 2011).

Since it is also a question of quantity, P loads from small STP generally contribute little to the annual P load. Furthermore, P levels from wastewater effluent water get diluted

when discharged to the river. However, higher concentration from small STP facilities coming in contact with sediments will lead to its higher TP.

The next question is whether the P levels in the river waters were significant in terms of adsorption/desorption potential. The earliest continuous river records for flow and P concentrations this author was able to find was for the station BE-O (S00-134) located on the Blue Earth River in Sibley Park, Mankato. This record contained river TP concentrations starting in 1967 to 1994 and some occasional records from 1997 to present (Fig. 17). The TP concentrations at this upstream location were generally higher than 0.2 mg/L with a peak concentration of 1.82 mg/L on March 7, 1978.

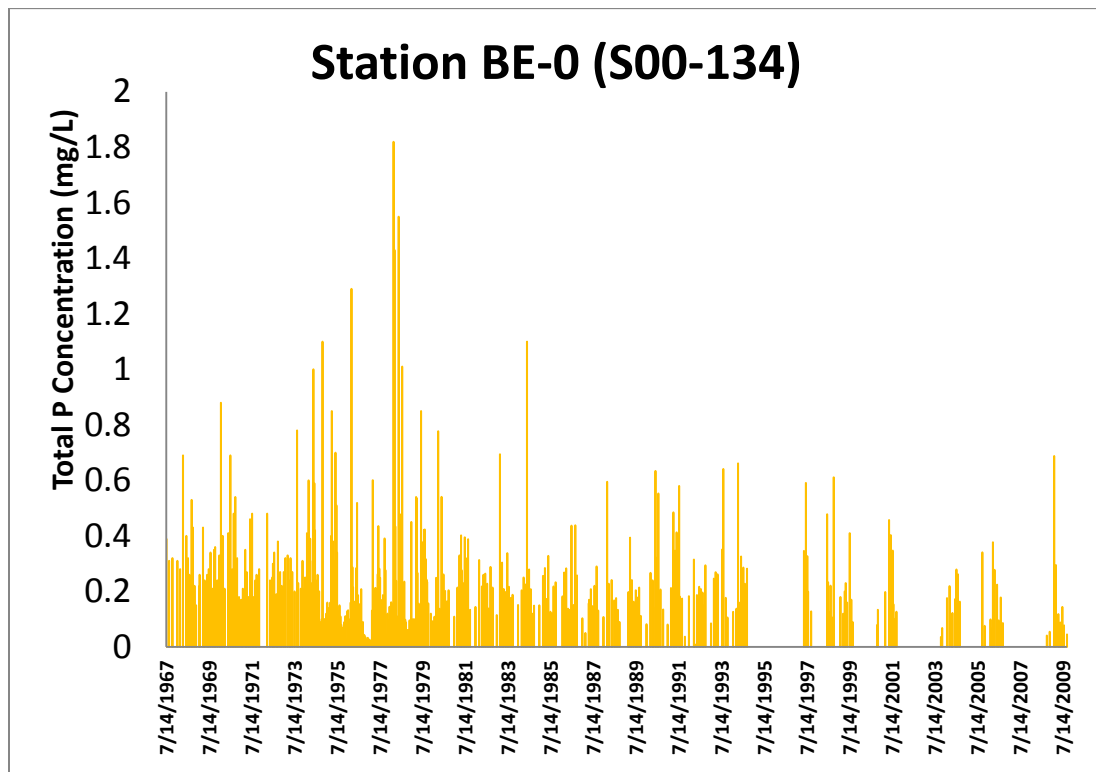


Figure 17. Continuous record of total P (TP) concentrations at a river gage located on the Blue Earth River in Sibley Park, Mankato (MPCA, 2011).

More recently, Johnson et al. (2009) reported the monthly flow weighted soluble P concentrations in the Minnesota River at Jordan and at Fort Snelling. These values are

based on the records from 1976-2003 at Jordan (Fig. 18a), and 1977-2003 records at Fort Snelling (Fig. 18b). The average monthly SRP concentrations in the Minnesota River at these two locations varied from 0.1-0.15 mg/L but the range was as high as 0.35 mg/L at Jordan and 0.45mg/L at Ft. Snelling (Johnson, 2009). Holmberg et al., (2004) analyzed USGS Elevation Derivative Applications (EDA) data, along with MPCA STORAGE and RETrieval (STORET) data, and USGS Long Term Resource Monitoring Program (LTRMP) data to compile annual flow weighted mean concentration of total bioavailable P in the Minnesota River at Fort Snelling from 1981 to 2001. During this 20 year time frame, total bioavailable P ranged from 0.1 mg/L at low flow to 0.146 mg/L at high flow. Information on the current level of P in river waters is important while assessing the potential of bank materials to adsorb or desorb P based on EPC_0 .

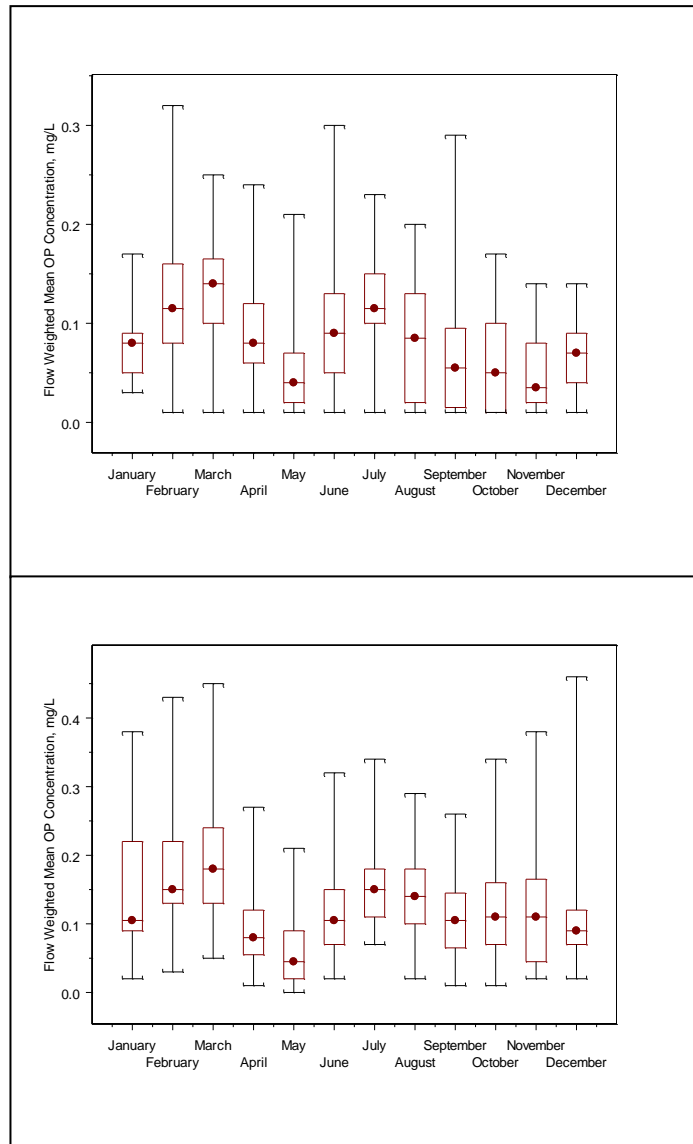


Figure 18. Monthly flow weighted soluble P (mg/L) in (a) the Minnesota River at Jordan (1979-2003) and (b) the Minnesota River at Fort Snelling (1977-2003) (Johnson, 2009)

From the river sediment perspective, the Army Corps of Engineers have also reported TP values. These concentrations vary from 79 to 561 mg/kg in samples of the dredged sediment taken from the Minnesota River (Table 5). The higher levels of TP in dredged sediments are an indication of high TP soil/bank material nearby or potentially adsorbed P from river water. On an average, TP of dredged sediments near the mouth of the Minnesota River varies between 200-300 mg/kg.

Table 5. Total P (TP) in dredged river sediments at various river miles (rm) along the Minnesota River (US Army Corps of Engineers, 2001).

Location	Date Year	TP mg/kg
AB Savage rm 14.5	1982	290
AB Savage RR rm 14.5	1982	230
AB Savage rm 14.5	1978	561
AB and BLW Cargill rm 13.2	1979	400
AB and BLW Cargill rm 13.2	1979	510
Cargill rm 12.9	2007	280
Above 35W rm 11.3	2007	270
Above 494 rm 4.3	2007	79
Below 494 rm 4.0	2007	220
Mouth of MN River rm 0.3	2007	450

Moving downstream along the Mississippi River towards Lake Pepin, the long term median TP concentration at Lock & Dam 1 is 90 µg/L. Below the confluence of the Minnesota and the Mississippi Rivers, the long term median TP concentration at Metro Plant at Lock & Dam 2 is 230 µg/L. Then the median TP concentration drops to 180 µg/L at Lock & Dam 3, or immediately below the confluence of Mississippi and the St. Croix Rivers (Larson, 1998). Finally, MPCA river gages have also documented historical TP levels gradually dropping both downstream and over time (Table 6).

Table 6. Total P (TP) from historical MPCA River gages along the Mississippi River upstream of Lake Pepin. TP concentrations in this table are not flow weighted as in Figure 18.

Year/Decade	Station ID	TP (mg/L)
67-68	S000-132	0.355
76-77	S000-132	0.295
88	Station 25- 001-00-258	0.352
89	S000-132	0.203
92	S000-132	0.191
2006	S000-132	0.088

Pearl button Industry and its implications on Lake Pepin Paleolimnological Records

Human activities such as point source pollution and the dredging requirements by the US Army Corps of Engineers have already been discussed in terms of their effect on water quality on river systems upstream of Lake Pepin. As we move downstream to Lake Pepin there have also been direct anthropogenic activities which have also altered the river environment and likely affected the Lake Pepin paleolimnological records. One of those alterations is the harvesting of mussels (Fig. 19) by the button industry. Listed below is a brief description of a mussel harvesting technique from Scarpino (1985).

“The pearl-button industry was the most prosperous between 1889 and 1916. After 1891 the industry sustained itself by continually expanding into new regions of the rivers. Many parts of the Mississippi were important sources of mussel shells until the mid-1920s. Lake Pepin in particular was a treasure trove, peaking at three to four thousand tons in 1914-1915 and at 2 thousand tons in 1924. In its bulletin from 1917-1918, the Bureau of Fisheries published an important analysis of the pearl-button industry in which the author explained, “Unquestionably Lake Pepin...has recently been yielding a greater quantity of shells per linear mile than any other stream or portion of a stream”. Mussels

were a “common property” resource-publicly owned and free to anyone who wished to collect them. Until the mid-1910’s, the harvesting of these valuable bivalves was largely unregulated...which contributed in a major way to the exhaustion of the resource. Technological developments that speeded up the gathering and the processing of shells also contributed to the destruction of the mussel fishery. In 1889, Hugh Smith, noted the recent invention of a device for taking mussels called the “crowfoot”. The crowfoot took advantage of the fact that mussels usually rested on streambeds partially buried in the bottom material. Mussel collectors lowered the crowfoot from a boat, floated downstream with the device dragging the bottom, and retrieved it covered with mussels closed tightly on the hooks. Fishermen could work deeper water with the crowfoot than they could with most other kinds of apparatus. In Lake Pepin, had very little current and an astonishing abundance of mussels, using motorboats to scour the riverbed with two to four crowfoot bars at the same time”.

The importance of this quote is that multiple actions have occurred in the Upper Midwest that may have disturbed the sediment record in Lake Pepin and thus made the paleolimnological records likely more difficult to interpret.



Figure 19. An example of the mussels found in the Blue Earth River (18 August 2010).

Lake Pepin Water Quality

Within Lake Pepin, several studies have characterized water and sediment quality. Earlier, we described the results of Engstrom et al. (2009) paleolimnology study. Another significant water quality works are the results reported by Heiskary and Wasley (2011) for mean summer SRP and TP in Lake Pepin since 1985 (Figs. 20 and 21). Although there are some fluctuations in the data, overall the trend has been a decrease in both

concentrations over time. For SRP, this decline is best described with mean summer values. For example, the mean summer SRP concentrations varied from a high of 0.12 mg/L in mid-1980s-early 1990's to a high of 0.06 mg/L in recent years (2003-2009). Similarly, mean summer TP values of the lake water declined from a high of 0.25 mg/L in mid-1980s-early 1990's to a high of 0.16 mg/L in recent years (2003-2009). These authors suggested that although similar declines in TSS and TP have been observed in the Minnesota River in this past decade, these declines in lake water are likely due to reductions in P input from point sources upstream of Lake Pepin (Heiskary and Wasley, 2011).

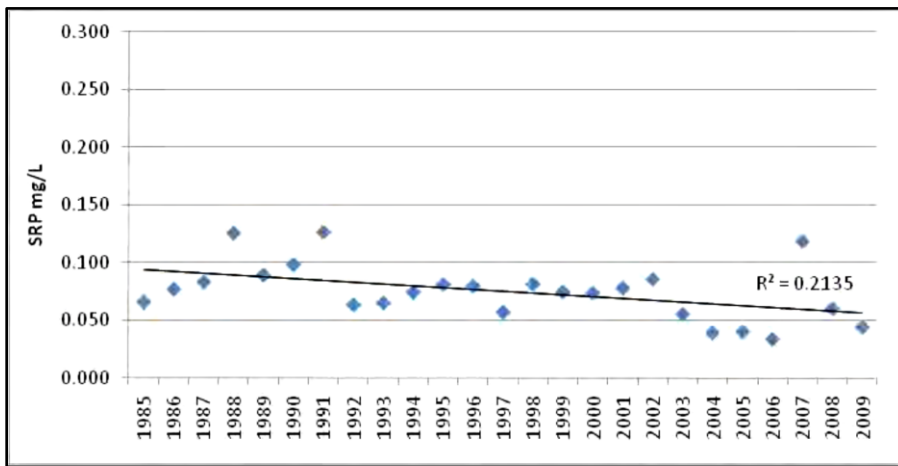


Figure 20. Temporal variation in mean summer soluble reactive P (SRP) concentrations in Lake Pepin (Heiskary and Wasley, 2011).

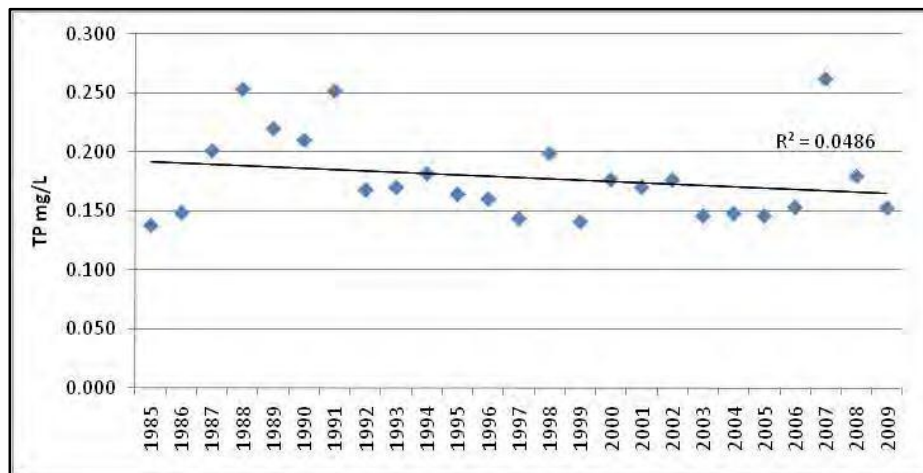


Figure 21. Temporal variation in mean summer total P (TP) concentrations in Lake Pepin (Heiskary and Wasley, 2011).

Based on computer simulation models and measured data, Heiskary and Wasley (2011) proposed the water quality goal of 100 µg TP/L for Lake Pepin. The downward trend in measured TP concentrations suggests that this is goal within the range of achieving. (Table 7). In 2009, the annual mean TP concentration in Lake Pepin was 152 µg/L (Table 7).

Table 7. Lake Pepin TP historical levels and policy goals (Heiskary and Wasley, 2011)

	2002 303(d) listing †	Recent 10 year mean ‡	2009 means	Criteria and goal ranges	Diatom-inferred P from 1900-1960 §
TP (ug/L)	198	171	152	80-120	~110-140

† 1991-2000

‡ 2000-2009

§ Estimate #1 (Engstrom and Almendinger 2000)

The P load in Lake Pepin consists of both water dissolved P as well as sediment attached P. Since the lake acts as a sink for sediments most of the sediment attached P remain in the lake. Based on input and outflow from the lake, James et al. (1998) estimated that only about 13% of the P input remained in Lake Pepin for the period 1994-1996. Most of this P was sediment attached P. The authors also reported substantial P loss (87%) from Lake Pepin via outflow; primarily in dissolved form.

Based on measured and estimated flow and the diatomic inferred P concentrations, Engstrom et al. (2009) showed that Lake Pepin P outflow increased from 700 t/yr in pre-settlement times to 2200 t/yr around 1900. After a slight decrease in 1920s and 1930s, P outflow again increased from 1900 t/yr to 2300 t/yr from 1940 to 1970. Present day P outflow from Lake Pepin is 4500 t/yr. Comparatively, sediment attached P loading in Lake Pepin increased from <100 t/yr in pre-settlement times to about 1000 t/yr. in present times. Sediment attached P loading was based on sediment load and the corresponding TP concentrations. Using the mass balance calculations, Engstrom et al. (2009) concluded that the percent of P retention in Lake Pepin has not remained constant over

time. Prior to 1830 the P retention in lake sediments was 7%. From 1830 to 1910, this retention increased to 10%. Starting around 1910, the percent of P retention dramatically rose to 16% and finally peaked at 32%. The current P retention rate has dropped down to 13% (James et al., 1998; Engstrom et al., 2009). A substantial portion of these increases appears to be linked to increased rates of sedimentation in Lake Pepin and also due to higher P concentration in the sediment.

In summary, SRP and TP levels are gradually decreasing in Lake Pepin. It has also been suggested that this is a reflection of upstream point source control. However due to changing climate, some of this decrease in water P concentrations may also be a reflection of changing climatic conditions. For example, Johnson et al. (2009) suggested that recent decrease in TSS, TP, and SRP concentrations in rivers may partially be the result of dilution from recent wet climate.

Climate Change Effects on River Flows

Extensive changes have occurred in the Minnesota River Basin, the main source of sediment and sediment attached P to Lake Pepin. Alterations include artificial drainage of poorly drained landscape as well as of some natural wetlands. McCorvie and Lant (1993) suggested that the net effect of these alterations is the efficient transfer of runoff from the landscape. Some have argued that these changes in drainage practices have contributed to earlier and greater runoff as observed in increased river flows. These arguments have been further stretched in that artificial drainage is leading to increased sediment load from river banks.

The single most important factor causing increased river flows is likely the changing climate. This in turn may be responsible for increased sediment load from both agricultural lands as well as river banks. For example, the large snowmelt floods on the Upper Mississippi River since about 1950 have enhanced the flux of sediments to the Mississippi River and downstream (Knox, 2001). This is in spite of the conservation efforts in recent decades. Mann et al. (1998) further suggested that climate change, specifically increased precipitation, is dramatically affecting sediment/nutrient transport by increasing the river discharge levels. Seeley (2006) suggested that since 1879, there

has been a gradual tendency for earlier occurrence of the annual maximum flood on the Mississippi River at Winona, MN (Seeley, 2006). The earlier occurrence of floods in recent years has been interpreted as a sign of global warming leading to rapid snowmelt.

In Minnesota the pattern of climate change can be described through four statistically significant trends in the last 30 years (Seeley, 2006): 1. Warmer winters, during which higher temperatures have been persistent and extensive. 2. Warmer minimum temperatures. 3. Increased episodes of higher summer dew points. 4. Greater annual precipitation. While all of these trends have strong implications for Minnesota's climate and the environment, it is the trend in increased precipitation which has the most direct implications for research reported in this thesis i.e. transport of sediment and sediment attached P. Over the last 50 years, most climate stations in Minnesota have shown an increase in average annual precipitation that ranges from 1 to 4 inches (Seeley, 2006). Karl et al. (1996) reported that annual precipitation has increased 10% to 20% over much of the Upper Mississippi River Basin during the 20th century. However, certain geographic areas have also more extreme records. For example, the precipitation increase in the Twin Cities for the period 1971-2000 relative to 1921-1950 has amounted to 4.68 inches. For the same periods, the mean annual precipitation in Waseca, South Central MN, has increased by 7 inch (Seeley, 2006).

Two types of precipitation are contributing to river flow increases: greater winter snowfall and more frequent and intense thunderstorm rainfall. In general, Minnesota has experienced a greater volume of snow annually. Records from 1890-2000 show an increase in annual snowfall of as much as 10 to 20 inches. This added snowfall and its fluid equivalent mean greater run-off volumes during the spring melt period. It is for this reason that many Minnesota streams have consistently shown higher measured volumes in the spring, often at or above flood stage.

Precipitation affects not only the river stages but also the type of P being transported. Larson et al. (2002) described that during low river flows, such as in 1988, point sources contributed to the majority of P loads to Lake Pepin. Model calculations showed that

89% of the P load during the summer of 1988 was from point sources. This assumed that all the effluent was transported downstream and not sequestered upstream. When river flows are high such as during flood or storm flow, non-points sources dominate the P loads. Investigations have also shown that during the average flow, the P pools are more evenly disturbed in terms of sources (Larson et al., 2002; Sharpley et al., 2008).

Materials and Methods

Study Area

The geological settings of Blue Earth County has been well described by Bennett and Hurst (1907) and Wright (1972a,b). Briefly, the area was glaciated by the Des Moines Lobe during the Wisconsin glaciations approximately 12,000 years before present and predominately consists of fine-textured, carbonate-rich buff colored glacial tills deposited by the Des Moines Lobe. In some places the till soil is as thick as 80 meters. With the retreat of the glacier, a large lake called Glacial Lake Minnesota formed in the Greater Blue Earth Basin. During the Holocene period Glacial Lake Minnesota covered this area with as much as 1 meter of the lacustrine sediments deposited on top of the till. The surface soils are black loam to fine clays with high organic matter content derived from prairie grasses native to the region. After glaciation and drainage of Glacial Lake Minnesota, river incision began. Currently, all the rivers in Blue Earth County are deeply incised with actively sloughing banks. The deep incision of these rivers is due to continuous down cutting after the River Warren drained the melt waters of Lake Agassiz and stranded the tributaries in this and other counties in the Minnesota River Basin from its master stream, the Minnesota River (Clayton and Moran, 1983; Gran et al., 2009). Today some of the river bottoms contain thin (< 2 m) deposits of alluvium material (Bennett and Hurst, 1907; Wright 1972a,b; Kelley et al., 2006).

Collection of Bank Materials and Soil Samples

A total of thirty-eight river bank materials representing till, lacustrine, and alluvium parent materials were collected from various depths and locations in Blue Earth County. Twenty six of these samples were collected by Dr. Holly Dolliver of the University of Wisconsin, River Falls. The procedure involved cleaning the face of the exposed bank and collecting the bank material from the desired depth. The remaining twelve river bank materials were collected by the author during field visits. These samples were taken from freshly slumped material to best represent the type of material falling into the river systems. Samples were not taken from material that had already fallen into the river.

Figure 22 shows the location of bank material sampling while Table 8 lists the location and origin of bank material samples tested in this study.

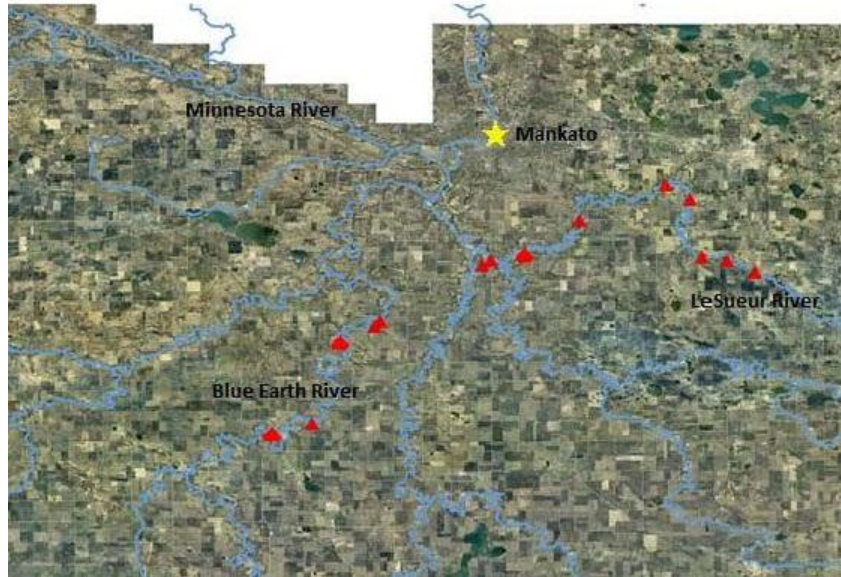


Figure 22. Locations of river bank material samples collected from Blue Earth County for P adsorption studies.

Table 8. Sample ID, parent material, location, and date of collection of river bank materials.

Sample ID	Parent Material	Location	Sample Collection Date
100	Till	Blue Earth River	8/22/2009
101	Miscellaneous	Blue Earth River	8/22/2009
102	Till	Blue Earth River	8/22/2009
103	Till	Blue Earth River	8/22/2009
104	Miscellaneous	Blue Earth River	8/22/2009
105	Miscellaneous	Blue Earth River	8/22/2009
106	Till	Blue Earth River	8/22/2009
107	Alluvium	Le Sueur River	8/9/2009
108	Alluvium	Le Sueur River	8/9/2009
109	Alluvium/Lacustrine	Le Sueur River	8/9/2009
110	Lacustrine	Le Sueur River	8/9/2009
111	Alluvium	Le Sueur River	8/9/2009
112	Till	Le Sueur River	8/9/2009
113	Lacustrine	Le Sueur River	8/9/2009
114	Miscellaneous	Le Sueur River	8/9/2009
115	Lacustrine	Le Sueur River	8/9/2009

116	Till	Le Sueur River	8/9/2009
117	Till	Le Sueur River	8/9/2009
118	Lacustrine	Le Sueur River	8/9/2009
119	Lacustrine	Le Sueur River	7/27/2009
120	Till	Blue Earth River	8/9/2009
121	Till	Le Sueur River	7/27/2009
122	Till	Le Sueur River	7/27/2009
123	Till	Le Sueur River	7/27/2009
124	Till	Blue Earth River	7/27/2009
125	Till	Blue Earth/Ulm Blend	7/27/2009
126	Till	Le Sueur River	7/27/2009
127	Till	Mankato Upland	8/22/2009
128	Alluvium	Le Sueur River	8/23/2009
129	Lacustrine	Blue Earth River	6/16/2010
130	Till	Blue Earth River	6/28/2010
131	Till	Blue Earth River	6/28/2010
132	Lacustrine	Blue Earth River	8/18/2010
133	Lacustrine	Blue Earth River	8/18/2010
134	Lacustrine	Blue Earth River	8/18/2010
135	Till	Blue Earth River	9/30/2010
136	Alluvium	Blue Earth River	9/30/2010
137	Alluvium	Blue Earth River	9/30/2010

In addition to river bank materials, surface samples of prairie soils were also gathered from twelve locations in the Minnesota River Basin. Virgin prairie soils refer to soil samples that were collected from lands that have never been farmed (Jeffers Petroglyph, Brown County) or lands that have been converted back into prairies. Table 9 lists the location of prairie soil samples.

Table 9. Prairie Soil collection date and their locations.

Sample Number	Sample Collection Date	Sample Description/ID
A	10/11/2010	Lindgren Prairie Martin Co. Fox Lake, Twp. Sec 9
B	10/11/2010	Delton Town Hall, Cottonwood Co, Delton, Twp. Sec 28
C	10/11/2010	Tony Thompson, Cottonwood Co, MTN Lake, Twp. sec 13
D	10/11/2010	Kimball Town Hall, Jackson Co, Kimball Twp. Sec 15
E	10/11/2010	Jay Town Hall, Martin Co, Jay,

		Twp. sec 16
F	9/14/2010	Lac qui Parle City Park (A), Lac qui Parle Co, Twp. Sec 27
G	9/14/2010	Lac qui Parle City Park (B), Lac qui Parle Co, Twp. Sec 27
H	9/14/2010	Lac qui Parle City Park (C), Lac qui Parle Co, Twp. Sec 27
I	9/14/2010	Lac qui Parle City Park (D), Lac qui Parle Co, Twp. Sec 27
J	9/17/2010	Jeffers Petroglyph (1), Brown Co, Mulligan Twp. Sec 12
K	9/17/2010	Jeffers Petroglyph (2) Brown Co, Mulligan Twp. Sec 12
L	9/17/2010	Jeffers Petroglyph (3) Brown Co, Mulligan Twp. Sec 12

Surface samples were also collected from six agricultural fields in the vicinity of the Blue Earth River. These fields were under corn and soybean rotation. Agricultural fields were randomly selected during our field visit to the county and several of these fields were close to a hog producing facility. The author presumed these fields have received some hog manure applications in the past. A brief description of these samples, without the exact locations due to privacy concerns, is given in Table 10. All bank materials, and surface prairie and agricultural soils were air dried, ground, and sieved through a 2 mm sieve prior to any chemical analysis including adsorption-desorption tests.

Table 10. Sample ID, date of collection, and the field usage at the time of sampling for surface soils from agricultural fields.

Agricultural Field Sample ID	Sample Collection Date	Field Usage
R	11/5/2010	Corn
S	11/5/2010	Corn
T	11/5/2010	Soybean
U	11/5/2010	Corn
V	11/5/2010	Soybean
W	11/5/2010	Corn

In addition to the bank materials listed above, samples were also collected from five deep cores taken by the Minnesota Geological Survey in Blue Earth County and currently

archived at the Department of Natural Resource (DNR) Facility in Hibbing, MN (Fig. 23). Deep soil cores were sampled to address the issue of variability in bank material properties with soil depth. It was assumed that the samples from these cores represent tall river banks that are not easily and safely accessible for sampling. The samples from core #8 were also analyzed for TP, bulk density, and particle size distribution. Other core samples were only analyzed for bulk density. Locations of the cores are shown in Fig. 24.



Figure 23. Photo of soil core containers at the DNR facility in Hibbing, MN taken 6 June 2011.

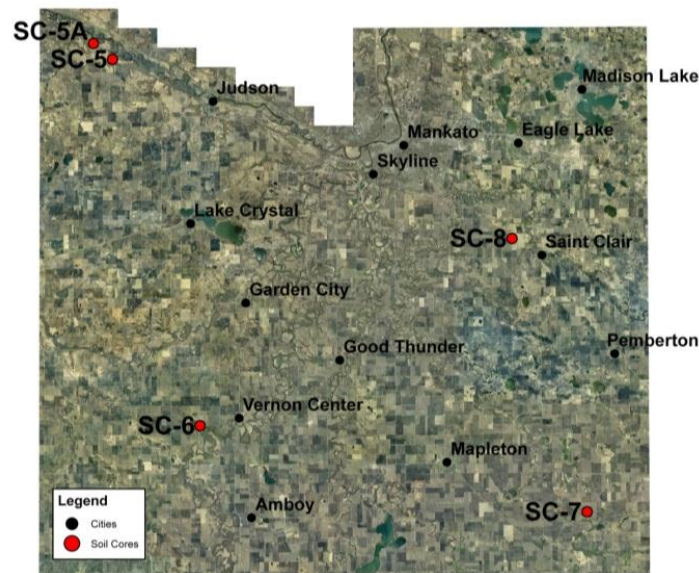


Figure 24. Location of deep soil cores collected by the Minnesota Geological Survey in Blue Earth County.

In order to address P remaining behind in the river systems, random samples were also collected from sand bars within the GBERB (Fig. 25) and a stored dredged materials site along the Minnesota River in Savage, MN (Fig. 26) The dredged material at Savage was removed upstream of the Minnesota/Mississippi confluence in 2010 and 2011. All samples were air dried, sieved through a 2 mm sieve, and then tested for basic soil tests parameters.



Figure 25. A sand bar along the Le Sueur River from where samples were collected for P testing.



Figure 26. A dredge material pile (lower right) in Savage, MN from where samples were collected for P testing. The Minnesota River can be seen in the background.

Soil Characterization

Bank materials, surface prairie, and surface agricultural soils were characterized for soil physical and chemical properties such as bulk density, particle size distribution, water pH, Bray and Olsen P, TP, loss-on-ignition, $\text{NH}_4\text{OAc-K}$, and 0.01M CaCl_2 extractable $\text{PO}_4\text{-P}$. Both particle size analysis and standard soil tests were performed by the University of Minnesota Soil Testing Laboratory. Standard soil tests followed the EPA standard procedures. Soil pH was determined in a 1:1 suspension (5 gram scoop of soil to 5 milliliters water) using a glass and a reference electrode with a pH meter.

Bulk density of the bank materials and soil samples was determined using the clod method (Blake and Hartge, 1986). Briefly, the procedure involved coating a 10-35 gram soil clod with paraffin wax at around 60 °C and then measuring its volume by recording the weight loss when suspended in water.

Particle size analysis was done using the Bouyoucos Hydrometer method adapted from Gee and Bauder (1986). Briefly, the procedure involved weighing 50 gram of dried, sieved soil in a 125 mL plastic bottle, and then dispersing the sample using a combination of chemical and physical methods. Chemical method included addition of 100 mL of 5% sodium hexametaphosphate (HMP) as a dispersing agent 12 hours prior to preparation of suspension. Physical methods included shaking the suspension for 12 hours. The suspension is then transferred to a 1000 mL cylinder. Particle amounts were determined by measuring the density of the suspension at various times using a hydrometer. The times for hydrometer readings (suspension densities) were: 40 seconds to determine the clay and silt fractions and 6.5 to 8 hours to determine the clay fraction. Suspension densities were corrected for temperature effects by taking the hydrometer reading of pure water.

Loss on ignition (LOI) is a method used to determine the amount of organic matter in soils. Briefly, the procedure involves heating a 5 gram scoop of the soil sample at 360°C

for 2 hours in a muffle furnace, and then calculating the loss in weight as a percent of the original sample weight.

Bray P test was developed by Roger Bray and Toubly Kurtz (Bray and Kurtz, 1945) at the Illinois Agricultural Experiment Station. The P extracted by this method correlates well with crop yield responses on most acid and neutral soils in the Midwestern United States. The procedure involves taking a 1 g scoop of soil, adding 10 milliliters of extractant, then shaking the suspension for 5 minutes, and measuring the soluble P. The extractant for this test is a solution consisting of 0.025 normal HCl and 0.03 normal NH_4F . The amount of phosphorus extracted is then determined by mixing the ascorbic acid and measuring the color intensity with an absorption spectrophotometer set at 640 nm. The results are reported in parts per million (ppm) P in the soil. For acidic soils the fluoride creates various aluminum/iron complexes in the solution, which releases the aluminum bound-P into the solution. The fluoride also inhibits re-adsorption of P onto the soil colloids. The acidic nature of the extract (pH 2.6) also enhances the dissolution of available P from aluminum, calcium, and iron bound forms. The upper limit for this test is 100 ppm (Bray and Kurtz, 1945) Table 11 lists various ranges of Bray P test values and the corresponding ranking of P availability to plants for Minnesota.

Bray P test is not suitable for clay soils with a moderate to high degree of base saturation, silty clay loam or finer-textured soils that are calcareous and have a pH > 6.8, or soils with a strong calcium carbonate equivalent (> 2% CaCO_3) (Kovar and Pierzynski, 2009). Since many of our bank materials and soils fit the above exceptions, we also ran Olsen P test on our samples

Olsen P test or sodium bicarbonate soil test P method was developed by Sterling R. Olsen in 1954. It was created to help predict crops response to applied fertilizer on calcareous soils (pH greater than 7.4). It is primarily used in North Central and Western United States. The procedure involves shaking a 1 gram scoop of soil with 20 milliliters of 0.5 molar sodium bicarbonate (NaHCO_3) solution for 30 minutes and then determining the

amount of phosphorus extracted using the ascorbic acid indicator method with a fiberoptic colorimeter probe set at 882 nm.

This method is based on principle that NaHCO_3 solution precipitates Ca^{2+} out into CaCO_3 complexes, thereby decreasing its concentration in the solution. This tying up of the Ca^{2+} enhances desorption of available P into solution. Results are expressed as ppm P in the soil. As with the Bray P test, potentially available organic P is also not measured by this test. The upper reporting limit for this test is 50 ppm. An Olsen P value of 10 mg P/kg is generally considered to be optimum for plant growth (Olson and Sommers, 1982; Recommended Chemical Procedures, 1988; Kovar and Pierzynski, 2009). Table 11 lists various ranges of Olsen P test values and corresponding ranking of P availability for plants in Minnesota.

Table 11. Various categories of plant available P and the corresponding Bray and Olsen soil test P values (Rehm et al., 2000).

Categories	Bray P	Olsen P
	-----ppm----- -	
Very Low	0-5	0-3
Low	6-10	4-7
Medium	11-15	8-11
High	16-20	12-15
Very High	21+	16+

Total Phosphorus (TP) refers to all forms of phosphorus in the soil. In order to measure this value, all forms of P in soil must be dissolved or released into the solution. This analysis is done according to the procedures suggested by Olsen and Sommers (1982) and the Soil Survey Laboratory Manual (1992). The procedure involves digesting the sample in nitric acid on a platinum block heated to 145°C for 1 hour. Next the sample is digested with perchloric acid and heated at 210°C for another hour, followed by analysis of the digest with the ascorbic acid indicator method using an absorption spectrophotometer set at 460 nm or a inductively coupled plasma atomic emission spectrometry (ICP-AES) (Olsen and Sommers, 1982; USDA, 1992).

Water Extractable P is also known as soil solution P which represents the portion of P that is dissolved and readily available for plant uptake. The procedure involves shaking 5 grams of soil with 50 mL 0.01 M CaCl_2 deionized water for 1 hour, centrifuging the suspension, obtaining the clear supernatant, and analyzing the P in the supernatant using the ascorbic acid indicator method with an absorption spectrometer set at 880 nm (Sparks et al., 1996).

Adsorption/Desorption Isotherms

The procedure for characterizing P adsorption and desorption by river bank materials and other soil samples was similar to the procedures used by Nair et al. (1984), Fang et al. (2002), James and Barko (2004), James and Larson (2008), and James (2010). Factors affecting P adsorption include soil/solution ratio, ionic strength, cationic species, shaking time, initial P concentrations, level of oxygen, rate and type of shaking, and the extent of solid/solution separation after equilibrium (Nair et al., 1984). Although most researchers use a similar basic procedure for characterizing P adsorption, there is considerable variation among studies with regards to the above parameters. This variation often makes comparisons of results difficult among studies. For this study, parameters were selected that best simulated the water conditions which bank materials or soil particles may experience during their river transport. For all our P adsorption tests, we used a 1:100 soil water ratio with 24 hour shaking time at room temperature varying from 22-25 °C. The water used in adsorption test was a dilute (0.005 M) CaCl_2 solution suggested by Lucci et al. (2010). This concentration is half that used by other investigators. Since there is some possibility that higher concentration of calcium in water may bind some of the desorbed P from soil particles, we selected 0.005 M CaCl_2 solution to minimize this possibility.

Mixing of the bank materials/soil samples and P solution in the adsorption test was done in a rotary mixer. pH readings of the suspension were measured both before and after mixing. The flowchart in Fig. 26 outlines the basic steps. Briefly, the adsorption procedure involved taking a small amount (0.45 grams) of bank material, shaking it with 45 mL of KH_2PO_4 solution of varying concentrations (0.0, 0.025, 0.05, 0.075, 0.1, 0.15,

0.2, 0.25, 0.5, 1.0, 2.5, 5.0, and 10.0 mg P/L) for 24 hours. All KH_2PO_4 solutions were made with 0.005 M CaCl_2 solution. The above P concentrations cover a range of total and soluble phosphorus measured by the Metropolitan Council of Environmental Services (MCES) in wastewater effluent or river waters. Previous research has shown that TP concentration in the Minnesota River varied from 0.04 to 1.80 mg/L at Jordan and 0.01 to 4.3 mg/L at Fort Snelling (Johnson, 2006). However, records also show TP concentration from waste treatment plants has been as high as 28 mg/L (FWPCA, 1966). In some cases, we also tested P adsorption from the river waters.

Following the mixing of bank material/soil sample with the P solution or river waters, suspensions were centrifuged for 30 minutes at 5500 rpm, filtered through a 0.45- μm filter into clean 50 mL plastic tubes, and then measure the P remaining in the solution. Sometimes after adsorption tests, desorption tests were also run on the same samples (Fig. 27). The desorption procedure involved weighing the wet solids after adsorption test, mixing proportional amount of 0.005 M CaCl_2 solution free of P, shaking the suspension for 24 hours, centrifuging the suspension for 30 minutes at 5500 rpm, filtering the decant through a 0.45- μm filter, and then measuring P released from the sediment.

Two tests involving three successive adsorption and desorption steps were also run on a subsample of four bank materials (100, 106, 113, 128). These tests are labeled Adsorption-Desorption-Adsorption (ADA) and Desorption-Adsorption-Desorption (DAD) (Figs. 28 and 29). At each step, the bank material was equilibrated for 24 hours with a solution of known P concentration. All adsorption/desorption tests were run in triplicates.

Phosphorus concentration in the filtrate of all adsorption and desorption tests was measured using the ascorbic acid procedure (EPA method 365.2) and a Hach Dr/2400 spectrophotometer set at 880 nm (EPA method 8048). In all P analysis, a 10 mL of filtrate was analyzed. Although limits of P characterization by the method varied from 0.20-2.50 mg/L, all samples with P concentration > 1.0 mg/L were diluted before analysis. The amount of P adsorbed/desorbed was calculated from the initial and final P

concentrations in solution, the amount of soil used, mixing ratio, and the dilution factors, if any, used during the ascorbic acid procedure.

The ascorbic acid procedure utilizes a detection solution followed by absorbency readings with a mass spectrometer. This colorimetric procedure is based on the premise that ammonium molybdate and potassium antimony tartrate reacts with dilute SRP in an acid medium to form an antimony-phosphate-molybdate complex. The addition of ascorbic acid causes the solution to be reduced and an intense blue color develops which is proportional to the concentration of SRP in the water (Kovar and Pierzynski, 2009).

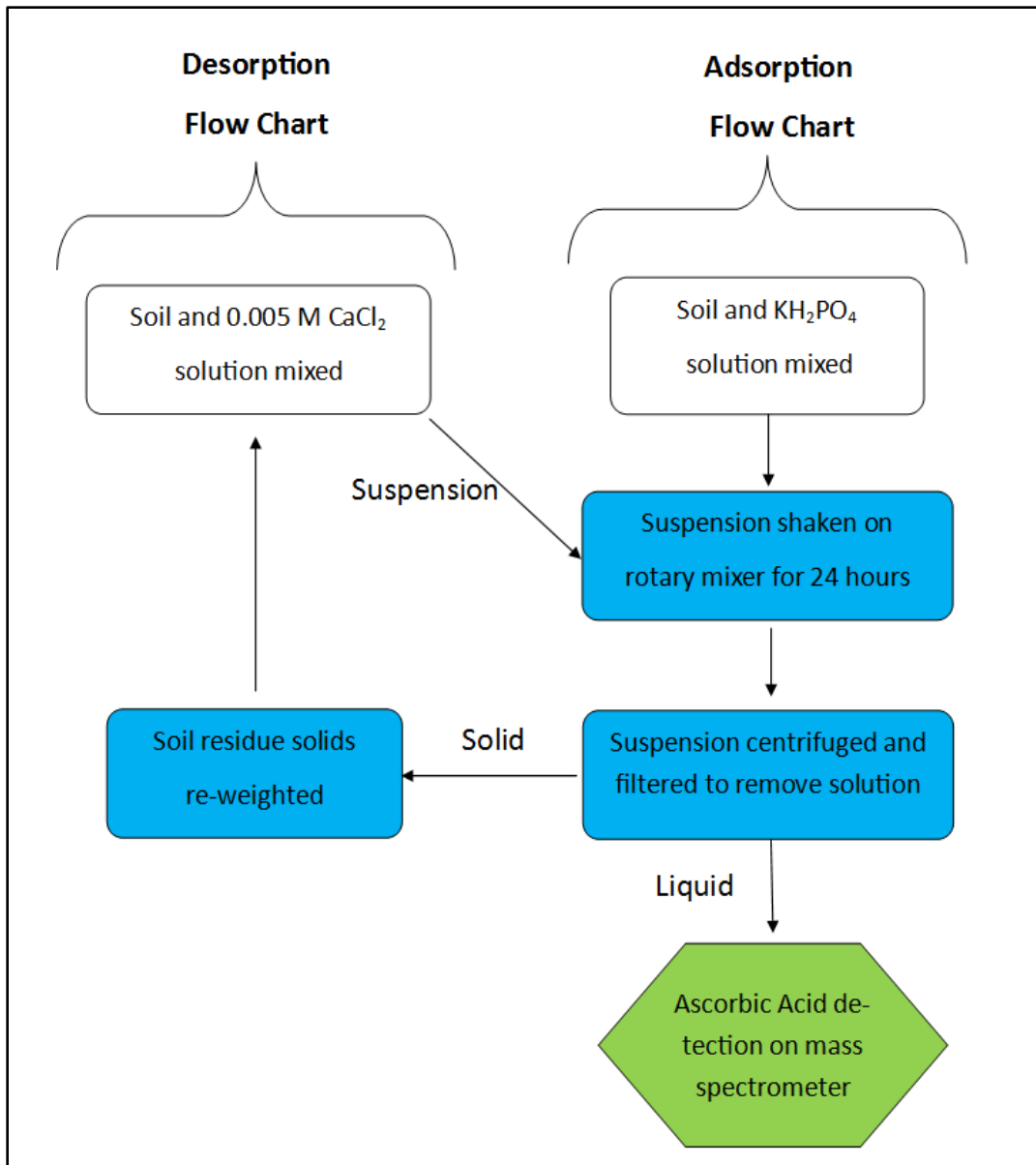


Figure 27. A flow chart describing the steps in the adsorption and desorption procedures.

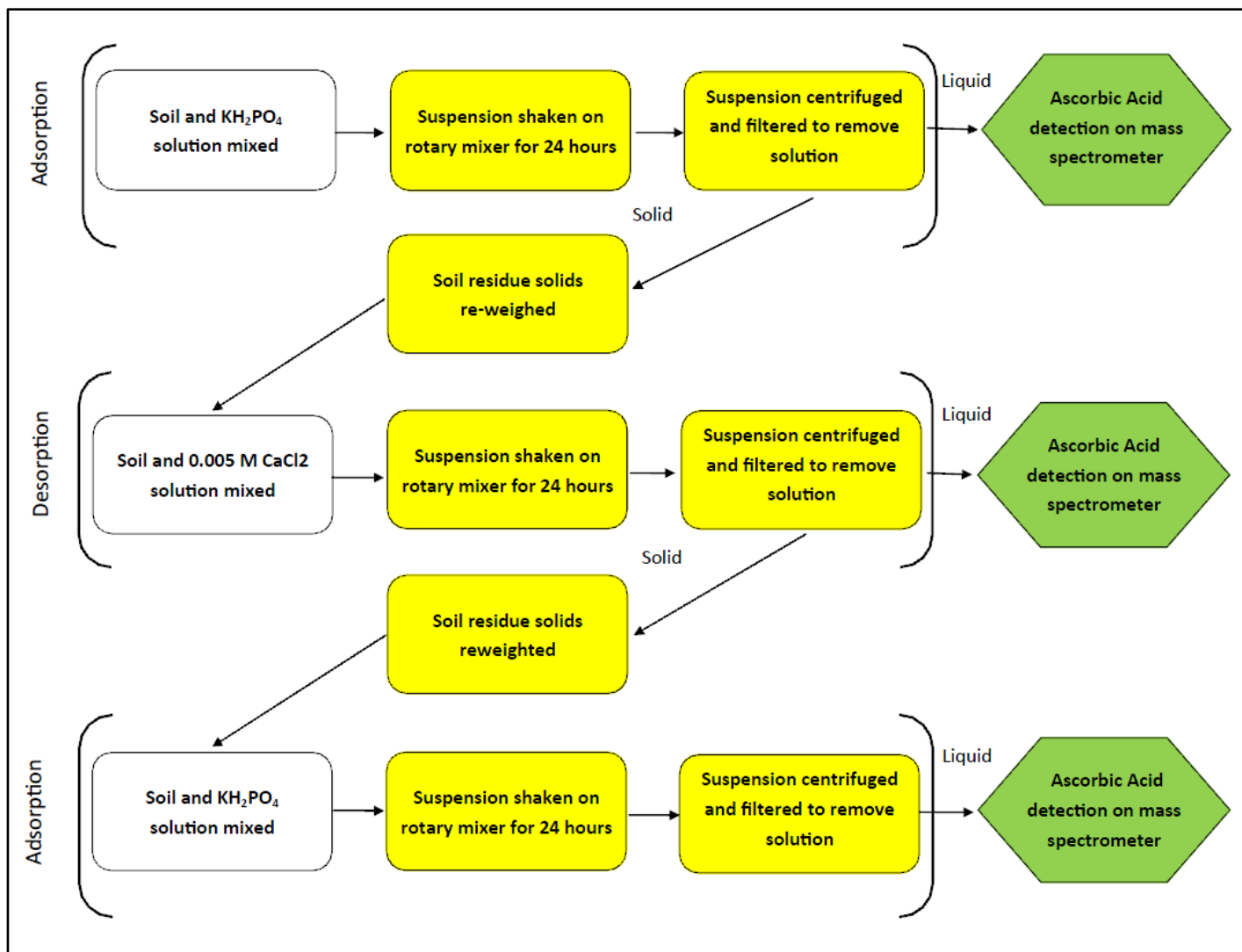


Figure 28. Flow chart showing Adsorption-Desorption-Adsorption (ADA), procedure.

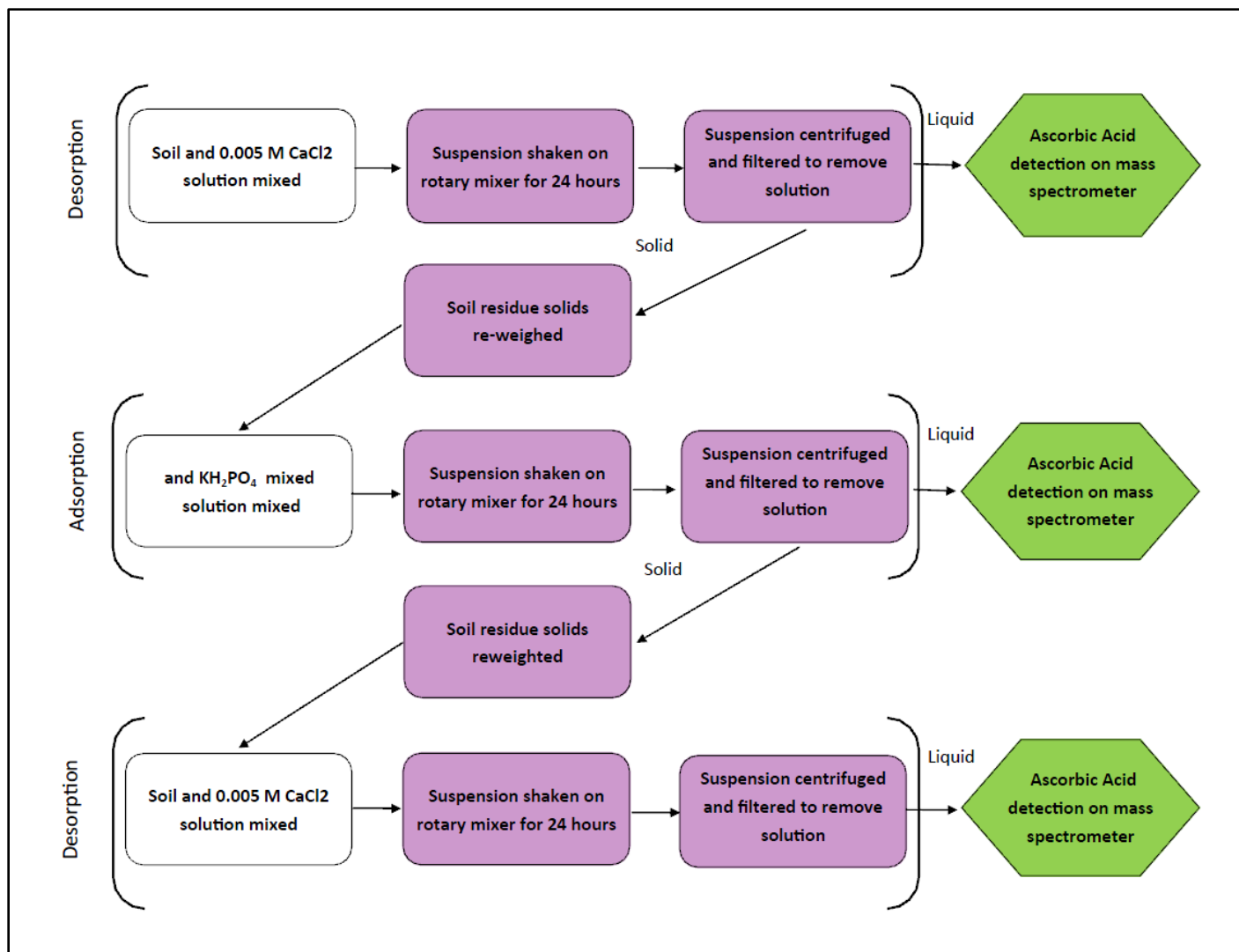


Figure 29. Flowchart showing Desorption-Adsorption-Desorption (DAD), procedure.

River Water Collection

Phosphorus adsorption by river bank materials and soils from river waters was also characterized for various river waters within the research watershed. These adsorption/desorption tests were run with natural river waters without the addition of KH_2PO_4 or 0.005 M CaCl_2 solution. The rivers include the Blue Earth River south of Vernon Center, the Maple River near Good Thunder, the Le Sueur River at Co. Rd. 8, the Minnesota River at County Hwy 22 by St. Peters, the Minnesota River at Hwy 19 in Henderson, the Mississippi River at Wabasha Bridge in St. Paul, and the Mississippi River at Prescott and Redwing. River waters were collected both during low flow (December) and high flow (June) periods using a surface grab method. Table 12 shows the dates and locations when river water samples were collected. A portion of each water sample was filtered through a 0.45 μm filter within 24 hours of collection and frozen for later analysis of SRP and running of the adsorption test. The above seasonal times when river water was collected also represented the low and high TP and SRP concentrations in rivers. Although total suspended solids (TSS) were also measured in these samples, the sediment in the grab samples generally is not representative of the entire water column.

At the start of this research, we also collected the water from the Minnesota River at Fort Snelling and used this water for some initial adsorption and desorption tests. The reason for initial selection of the Minnesota River water was that it represented the cationic strength, conductivity, and pH that the sediments will encounter as they are tumbling downstream. However, as this water contained small amounts of phosphorus and the subsequent difficulty of getting similar water each time over the two year study period, we abandoned this approach and used dilute (0.005M) CaCl_2 solution. We did compare the adsorption isotherms between tests that used 0.005 M CaCl_2 solution vs. the Minnesota River water, and the results were similar.

Table 12. Location and dates for river water sample collection.

Location	Dates of Collection				
	3/16/2011	6/17/2011	7/20/2011	9/20/2011	12/20/2011
Blue Earth River at Vernon Center	X	X		X	
Maple River at Good Thunder	X	X		X	X
Le Sueur River at Co. Rd 8	X	X		X	
Minnesota River at St. Peter	X	X		X	X
Minnesota River at Henderson					X
Mississippi River at Wabasha Bridge St. Paul			X		X
Mississippi River at Redwing			X		

Waste Water Collection

We also collected the waste water effluent samples from the sewage treatments plants in the study area. These sewage treatment plants were the Vernon Center plant in Vernon Center, Eagles Point in Cottage Grove, Hastings STP in Hastings, Seneca in Eagan, and Blue Lake in Shakopee. Due to time constraints most of the samples from the STPs were collected only once in July. In Table 13 are listed the dates the effluent samples were collected. The most extensive collection was from the Vernon Center treatment plant. A portion of each sample was filtered through a 0.45 μm filter within 24 hours of collection and then frozen for later analysis of SRP.

Table 13. Location and dates of effluent water sample collection from various waste water treatment plants in the study area.

Location	Dates of Collection				
	3/16/2011	6/17/2011	7/20/2011	9/20/2011	12/20/2011
Waste Treatment plant at Vernon Center	X	X		X	
Eagle Point WT Plant in Cottage Grove			X		
Seneca WT Plant at Eagan			X		
Blue Lake WT Plant at Shakopee			X		

Sequential Fractionation

For some of our bank materials and soil samples, we also ran a sequential fractionation to characterize various types of particulate P (PP). Part of this sequential analysis was run by the author and part by William James previously of US Army Corps of Engineers. In this study, sequential fractionation of PP was conducted according to methods proposed by Hjieltjes and Lijklema (1980) and Psenner and Puckso (1988). This technique has been used by James and Larson (2008) in analyzing suspended sediments from the Minnesota River. The fractions analyzed were the loosely bound-P, iron bound-P, labile organic-P (LOP), aluminum bound-P, calcium bound-P, and refractory organic-P. These fractions were sequentially extracted using ammonium chloride, bicarbonate-dithionate, sodium hydroxide, hydrochloric acid, and finally a persulfate digestion (Shang and Zelazny, 2008). In Table 14 are listed the chemicals used for extraction of various P fractions as well as the corresponding extraction mechanisms and the recycling potential of these fractions. Since NaOH also causes the hydrolysis of humic substances during aluminum bound P analysis, a subsample of the sodium hydroxide extract was further digested with potassium persulfate to quantify the non-reactive aluminum bound P. Labile organic P was calculated as the difference between reactive and non-reactive aluminum bound P. P remaining after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid to determine refractory organic P. Each extraction was filtered through a 0.45 µm filter and adjusted to pH 7 before being

analyzed for SRP using the ascorbic acid method. In general loosely bound P, iron bound P, and labile organic P are the biologically labile forms of P and thus more readily available for microbial use. Comparatively, the aluminum bound P, calcium bound P, and refractory organic P are non-labile forms and more subject to sediment burial (James and Barko, 2004).

Table 14. Various particulate P extraction fractions and the corresponding chemicals used for extraction (James and Barko, 2004; James and Larson, 2008; Shang and Zelazny, 2008).

Variable	Extractant	Extraction mechanisms and remarks	Recycling Potential
Loosely Bound P	1 M ammonium chloride	Dissolution and/or mass action displacement by Cl^-	Biologically labile: recycled via eH and pH reactions and equilibrium processes
Iron Bound P	0.11 M sodium bicarbonate-dithionate	By removing free Fe oxides by reduction of Fe^{+3} , **Incomplete dissolution of Fe oxides in large particle sizes	Biologically labile: recycled via eH and pH reactions and equilibrium processes
Aluminum Bound P	0.1 N sodium hydroxide-followed by persulfate digestion	Desorption from various adsorption sites; and hydrolysis of humic substances; subsample with persulfate for non-reactive	Biologically Refractory
Labile Organic P	Persulfate digestion of the NaOH extraction	Difference between reactive and nonreactive aluminum bound P	Biologically labile: recycled via bacterial mineralization of organic P and mobilization of polyphosphates stored in cells
Calcium Bound P	0.5 N hydrochloric acid	Acid dissolution of carbonates and apatite including detrital apatite	Biologically Refractory
Refractory Organic P	Persulfate digestion of remaining particulate P		Biologically Refractory

Finally, we were also interested in exploring how TP may be distributed among various size particles in the bank materials as this relates to particle enrichment when the coarser fraction such as sand is left behind in sand bar/depositional features. In order to quantify P in various particle fractions, particles had to be separated by size fractions and then analyzed separately. The bank material chosen for this analysis was till sample #100. The fractionation of various size particles involved oxidizing organic matter of the sample with H_2O_2 , destroying the calcium bonds with HCl, suspending the bank material in a 0.005 M $CaCl_2$ solution that was also buffered with 0.076 mg/L P as KH_2PO_4 . This specific chemical solution was chosen to simulate the ion levels of the river water as well as try and maintain the P concentrations on the individual particles during particle fractionation. Following the chemical pre-treatment, the sample was suspended in the 0.005 M $CaCl_2$ solution and sand fraction separated using a 50 mm sieve. Remaining suspension of each sample was poured in a one liter cylinder and finer particles (silt and clay) were separated based on the settling time of particles calculated from Stokes law. Details of this procedure are described by James (2010). After particle separation, the samples were sent to the University of Wisconsin, Soil Testing Laboratory in Madison, WI for TP analysis.

Statistical Methods

Data were evaluated using Statistical package in Excel (Microsoft Office, 2009). Statistical significance for all procedures was tested at a probability level of 0.05.

Results and Discussion

Soil Test Characterization

The soil test characterization of various bank materials and surface soils used in this study are summarized in Tables 15-19. The soil characterization included Bray and Olsen P tests, pH, OM, bulk density, particle sizes, SRP, and TP. Bank materials data are summarized into three groups based on the type of parent material (Till, Alluvium, and Lacustrine) whereas surface soils are summarized into two groups based on current land use (agricultural soils and prairie soils).

Soil P Tests: As mentioned earlier, Bray P correlates well with crop yield response on most acidic and neutral soils whereas Olsen P correlates well with crop yield response on alkaline and calcareous soils. Both of these tests characterize slightly different fractions of TP. Considering bank materials and soils in the Minnesota River Basin are calcareous in origin, Olsen P test is a better indicator of P availability to plants from these soils. In general, Bray and Olsen soil test P values are low for bank materials and prairie soils compared to the agricultural soils tested in this study (Table 15). Within the bank materials, the soil P test values are the lowest for till, followed by lacustrine, and alluvium materials. The low Olsen P test values for most bank materials and surface prairie soils suggest that additional P applications will be needed on these materials should they be used for growing agricultural crops. As expected, there is no definitive relationship between Bray and Olsen soil P test values for these materials (Fig. 30). In our study, high soils test P levels found in the agricultural soils is mainly because these soils were collected from an area where hog manure has likely been applied.

Table 15. Bray and Olsen soil P test values (average \pm standard deviation) grouped by parent material type for bank materials and by land use for surface soils.

Bank Material/Soil	Bray P	Olsen P
	-----ppm-----	
Till Banks	1.50 \pm 1.47	5.69 \pm 4.77
Lacustrine Banks	1.67 \pm 1.41	6.75 \pm 8.53
Alluvium Banks	10.57 \pm 8.58	11.86 \pm 6.31
Miscellaneous Banks	5.25 \pm 4.99	8.33 \pm 5.86
Surface Prairie Soils	3.67 \pm 4.48	6.42 \pm 5.68
Surface Agricultural	56.07 \pm 32.16	20.75 \pm 14.73

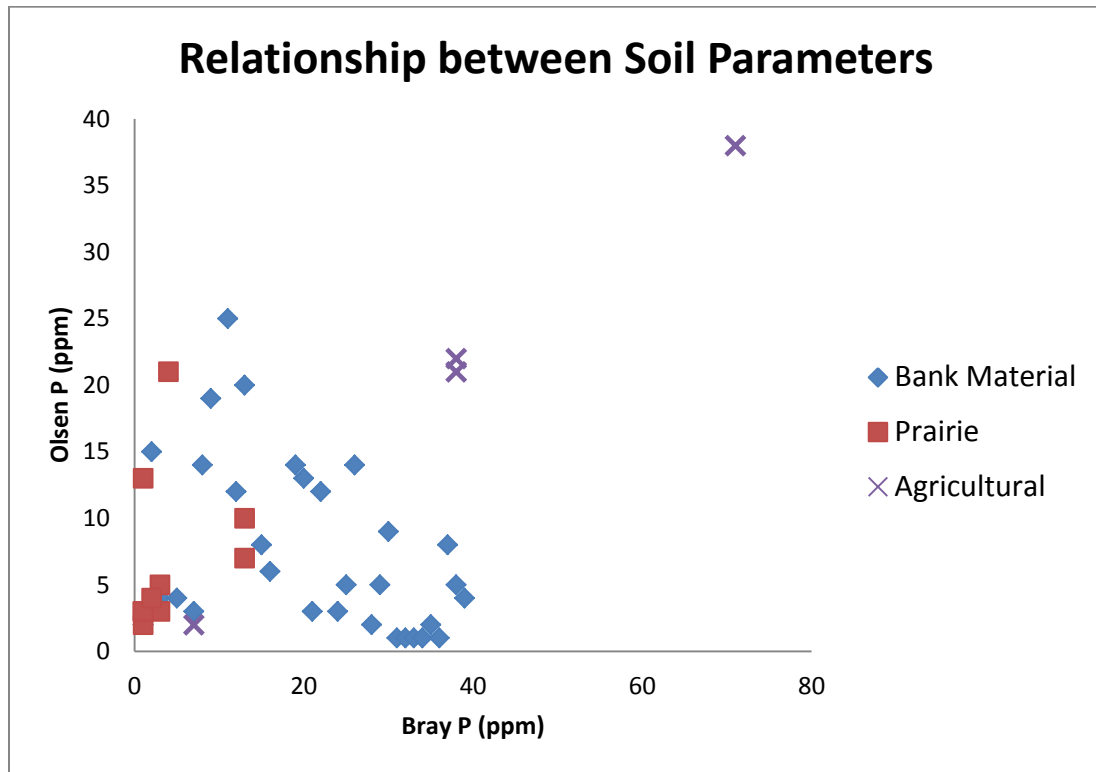


Figure 30. Relationship between Olsen P and Bray P test values for bank materials and surface soils tested in this study.

Soil pH: Phosphorus adsorption and desorption and in turn P availability is highly dependent on soil pH. In acid soils, iron and aluminum form more stable P compounds whereas in alkaline soils calcium forms more stable P compound. It is for this reason, the greatest ability of a soil to adsorb and retain P occurs at very low and very high soil pH values. In contrast, at more normal pH values there is a greater potential for the release of these bound phosphates. For example as the pH increases from 5 to 6, iron and aluminum P compounds become somewhat more soluble (Brady and Weil, 1999). Similarly, lowering pH from 8 to 6 helps in the dissolution of calcium P compounds.

The chemical species of phosphorus present in a soil solution is also determined by the solution pH. In near neutral soils, the two dominant species are the monovalent (H_2PO_4^-) and the divalent (HPO_4^{2-}) anion. Both of these species are readily available for plant uptake. The general rule for optimum P availability to plants is when the soil pH ranges between 6 and 7 (Brady and Weil, 1999). Table 16 summarizes the variation in pH for bank materials and soils tested in this study. Since most of the bank materials and surface soils are derived from calcareous parent materials, pH of these samples are slightly above neutral.

Table 16. pH values (average \pm standard deviation) of bank materials grouped by parent material and of surface prairie and agricultural soils grouped by land use.

Bank Material/Soil	pH (Ave \pm SD)
Till Bank Materials	7.71 \pm .32
Lacustrine Bank Materials	7.64 \pm .73
Alluvium Bank Materials	7.71 \pm .36
Miscellaneous Bank Materials	7.33 \pm 1.02
Surface Prairie Soils	7.11 \pm .82
Surface Agricultural Soils	7.31 \pm .82

Loss on Ignition (LOI): Loss on ignition is an indicator of the organic matter (OM) content of the soil and bank materials. Organic matter itself generally has little capacity to strongly fix P ions but it is associated with labile P and increases the availability of loosely bound P for plant uptake. This is because organic anions and larger humic

molecules reduce the sites available for strongly fixing P. Organic acids may also capture reactive iron and aluminum into organic complexes, making these metals unavailable for reactions with P ions in solution. Generally, soils with high OM content show low levels of P fixation but high levels of available P (Brady and Weil, 1999).

Table 17 summarizes the OM content of various materials tested in this study. As expected, surface prairie soils have the highest OM, followed by surface agricultural soils, and then bank materials. Among the bank materials, lacustrine materials have higher OM content than the deeper tills and the alluvium materials. This is expected because prairies dominated the lacustrine surface materials whereas till samples are the buried materials.

Table 17. Organic matter content (average \pm standard deviation) of various bank materials and surface soils as measured by loss-on-ignition.

Bank Material/Soils	OM %
Till Bank Materials	0.91 \pm 0.38
Lacustrine Bank Materials	2.89 \pm 4.17
Alluvium Bank Materials	0.73 \pm 0.39
Miscellaneous Bank Materials	2.20 \pm 2.20
Surface Prairie Soils	6.47 \pm 3.19
Surface Agricultural Soils	4.44 \pm 2.13

Bulk Density: The bulk density of the tills is the highest followed by alluvium and lacustrine bank materials, surface agricultural soils, miscellaneous bank materials, and surface prairie soils (Table 18). Higher bulk density of the tills is mainly because of the overburden that these materials have been subjected to during a series of glaciations. Comparatively, the bulk density of the prairie soils is the lowest because of higher organic matter content.

Table 18. Bulk density (average \pm standard deviation) of various bank materials and surface soils tested in this study.

Bank Material/Soils	Bulk Density, Mg/m ³
Till Bank Materials	1.86 \pm .15
Lacustrine Bank Materials	1.62 \pm .21
Alluvium Bank Materials	1.74 \pm .38
Miscellaneous Bank Materials	1.44 \pm .06
Surface Prairie Soils	1.35 \pm .14
Surface Agricultural Soils	1.72 \pm .06

Particle Size Distribution: Particle size analysis was performed on forty-seven samples that included all thirty eight bank materials and randomly selected surface prairie, and surface agricultural soils. A majority of both bank materials and surface soils belong to the loam, clay loam, and sandy loam textural groups (Fig. 31). A characterization of individual bank material based upon parent material is given in Appendix A (Figure A1).

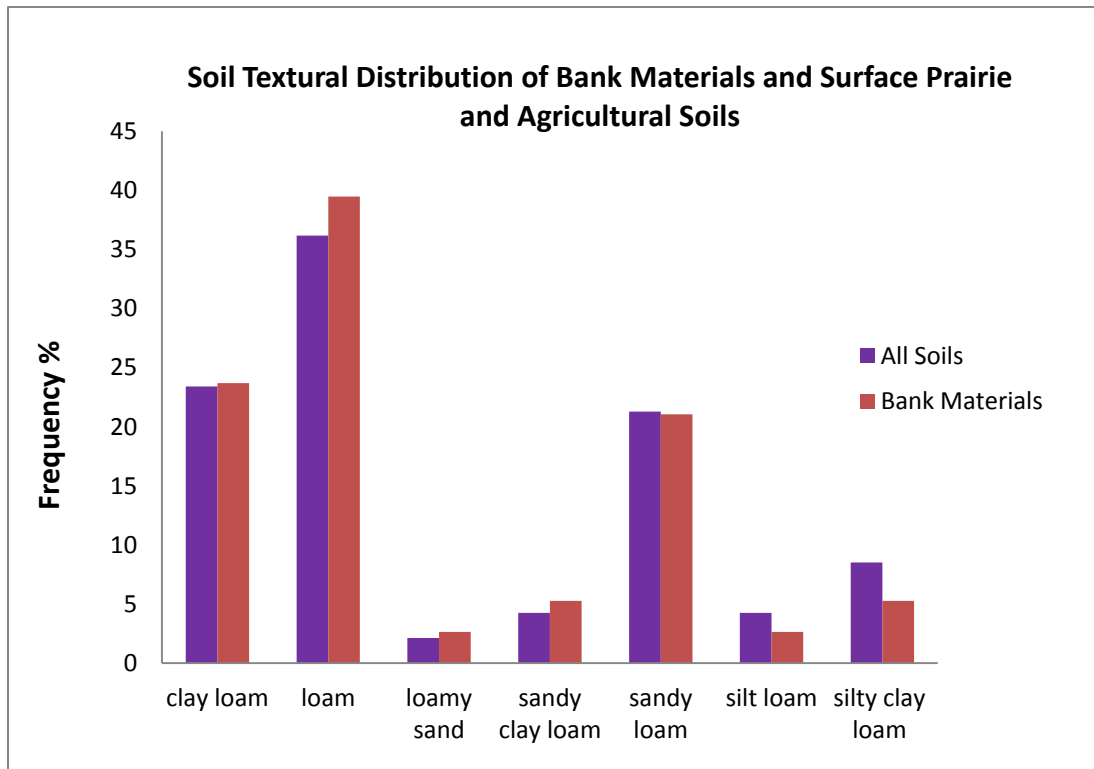


Figure 31. Textural Distribution of bank materials and surface prairie and agricultural soils.

Soluble Reactive P and Total P: Soluble reactive P (SRP) also called the extractable PO_4P is readily available to biological species including terrestrial and aquatic plants. In some cases, it has also been referred to as loosely bound P. This P is characterized by shaking the soil samples with 0.01 M CaCl_2 solution. Total P on the other hand comprises of all dissolved and particle bound fractions as well as organic and inorganic forms. To be comparable between various studies, TP concentrations are mainly used for establishing TMDL and record keeping.

In general, agricultural soils had the highest SRP and TP concentrations followed by the prairie soils, and then various bank materials (Table 19). The higher SRP and TP values in agricultural soils in this study are likely due to routine hog manure applications. The differences in SRP between the surface agricultural soil vs. the surface prairie soils or the bank materials are much more noticeable. This is likely due to hog manure applications on agricultural soils. Comparatively, TP values of surface soils are higher than the bank materials, mainly due to P recycling from vegetation in prairie soils and P addition from manure application in agricultural soils.

Table 19. Soluble reactive P (SRP) and total P (TP) (average \pm standard deviation) of various bank materials and surface soils tested in this study.

Bank Material/Soils	SRP	TP
	-----ppm-----	
Till Bank Materials	0.19 \pm 0.08	409 \pm 76
Lacustrine Bank Materials	0.17 \pm 0.09	488 \pm 106
Alluvium Bank Materials	0.30 \pm 0.15	477 \pm 180
Miscellaneous Bank Materials	0.37 \pm 0.38	450 \pm 50
Surface Prairie Soils	0.47 \pm 0.45	543 \pm 109
Surface Agricultural Soils	3.04 \pm 3.66	562 \pm 262

Overall there were no significant relationships between TP concentrations and Bray soil test P values, Olsen soil test P values, or LOI percent. However, a statistically significant relationship existed between TP and LOI for the surface prairie soils ($R^2 = 0.66$, $P = 4.12 \times 10^{-5}$, $N=14$) and between TP and SRP (Fig. 32) for surface agricultural soils ($R^2=0.71$, $P=0.008$, $N=8$). The higher correlation coefficient between TP and SRP in surface

agricultural soils is likely a reflection of regular hog manure applications on these soils as hog manures generally contain large quantities of readily available P and total P that potentially increases soil's TP values on manure application. The lack of statistical significant relationship between TP and SRP for bank materials or for prairie soils may be due to a small range of SRP values found in these materials.

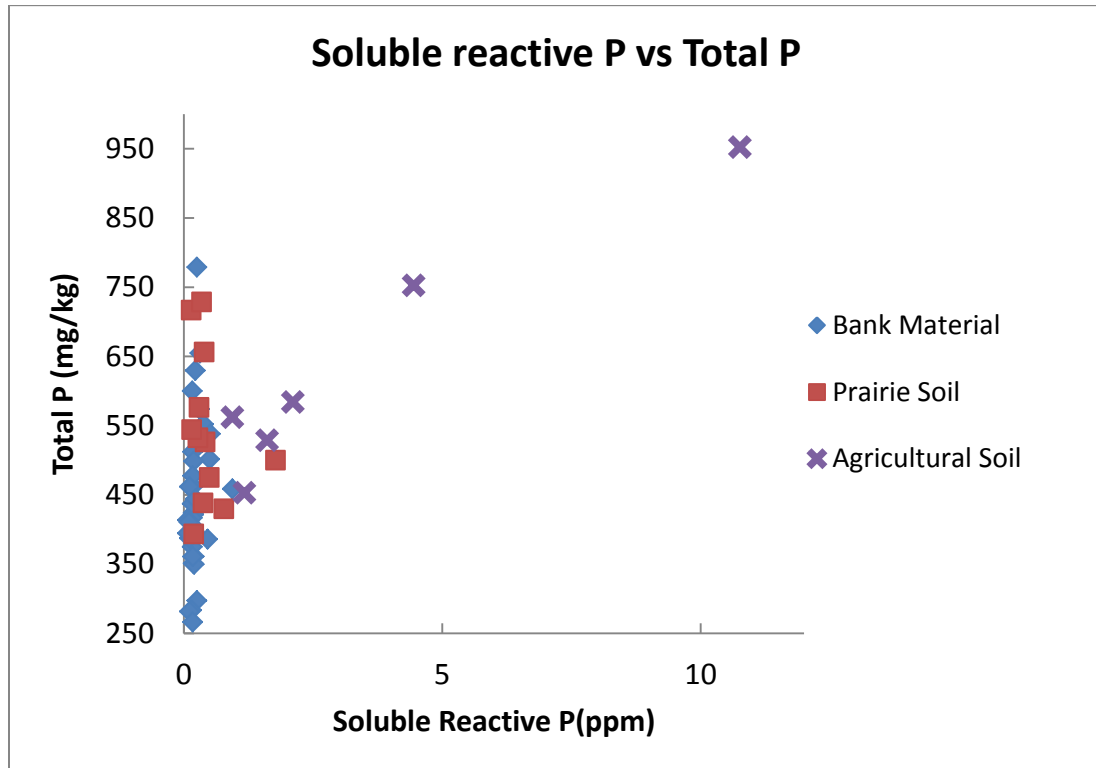


Figure 32. Relationship between total P (TP) and soluble reactive P (SRP) for bank materials and surface prairie and agricultural soils.

River Water and Effluent P Analysis

TP and SRP concentrations in river waters and effluents from various sewage treatment plants are summarized in Table 20. TP concentrations represent the TP concentration of the filtrate after sediments have been removed. The river waters have a wide range of SRP and TP concentrations due to differences in seasons when these samples were collected as well as due to differences in locations in a given river system. As expected,

the SRP levels are a significant portion of the TP in river waters since the sediments have been removed.

In both effluent and river water samples, most of the TP is made up of SRP but the range of TP and SRP concentrations is much higher in the effluent samples than in river waters. As stated earlier, concentration of P in STP effluent must be considered in the context of quantity released. Even though the Twin Cities STP effluents are lower in TP and SRP concentrations, total quantity of P released is very high due to large volume of effluent discharge. Based on the discharge monitoring reports (DMR) for the sewage treatment plants we sampled, these five facilities released 134.3 tons TP in 2011 (MPCA, 2012a). Since most of the TP in effluent is readily available for algal growth, the total quantity of P moving downstream has a greater impact on Lake Pepin water quality than the change in P concentration in river water. The importance of the river water P concentrations is more in the context of P adsorption by sediments as they are moving downstream. Furthermore, it may affect the EPC_0 of river sediments.

Table 20. Total P (TP) and soluble reactive P (SRP) in various river waters and effluents from sewage treatment plant

Water Type	TP Range (mg/L)	SRP Range (mg/L)
River Water	0.03-0.6	0.01-0.43
STP Facility Effluent	0.1-2.74	0.02-2.72

Adsorption-Desorption Studies

Desorption and Equilibration Time: A series of initial tests assessed the potential of bank materials to adsorb and desorb under various scenarios. Most of these initial tests were done with the Minnesota River water in order to simulate realistic conditions. The first set of experiments involved desorption over 7 days. This was done to evaluate the extent of desorption and whether or not the desorption process is instantaneous or continuous over a long period. In this experiment a series of bank materials were exposed for 7 days to the Minnesota River water from Fort Snelling. The water contained low levels of soluble phosphorus. Desorption was measured at several time increments by

subtracting the initial P concentration from the equilibrium P concentration in the river water at any given time. Figure 33 is a plot of P desorption as a function of time for four bank materials. The data shows that for all materials there was an initial rapid release/desorption of P. This rapid release occurred within ten minutes the samples were exposed to river water. This was followed by a very small P release (slow desorption) at subsequent time increments as indicated by relatively flat slope of the desorption curve. Although there were small differences in desorption behavior between different materials, total desorption was rather minimal. Similarly, we also ran adsorption tests and they showed that P adsorption was quite rapid with these materials. These initial studies showed that 24 hours equilibration time was sufficient for P desorption and adsorption. Based on these tests, sample-solution equilibration time of 24 hours was set in subsequent adsorption/desorption studies.

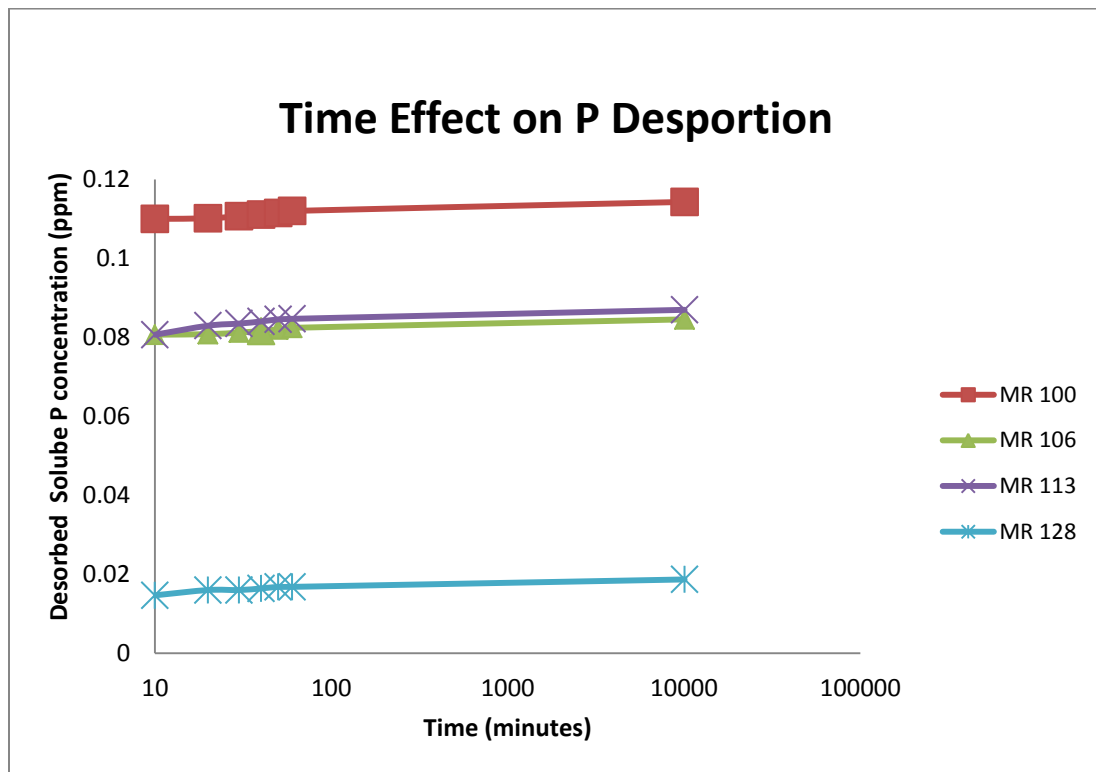


Figure 33. P desorption from four bank materials as a function of time in the Minnesota River water.

Adsorption-Desorption Sequences: In this experiment, a series of successive adsorption-desorption tests were run with high and low P CaCl₂ (0.005 M) solution. The three successive runs in this experiment were adsorption-desorption-adsorption (ADA) and desorption-adsorption-desorption (DAD). This experiment was done with four bank materials (100, 106, 113, 128), however only the results for bank material #100 are shown here. Results of bank material #100 are representative of the results from other three soils in this experiment. Results of all four bank materials are given in Appendix B, Figures B1 and B2. The results showed that in the first adsorption test, P adsorption on bank materials increased with an increase in solution P concentration (Figs. 34 and 35). This was similar to the behavior reported in other adsorption isotherm studies (Fang et al., 2002).

In the second round when the above samples were exposed to 0.005 M CaCl₂ solution only (desorption), there was very little P desorption. This was also the case even for samples that had been exposed to higher P concentrations in the previous adsorption test. Lack of any P desorption indicates a strong P binding ability of the bank materials. In the third round when the above samples were again subjected to P containing CaCl₂ solution (similar to step #1), there was some additional P adsorption which increased with an increase in solution P concentration. These results suggest that when subjecting the bank materials to alternating adsorption/desorption/adsorption processes, there is minimal desorption and some slight additional adsorption in the second adsorption round. Perhaps this additional adsorption indicates adsorption beyond the initial surface charge attraction.

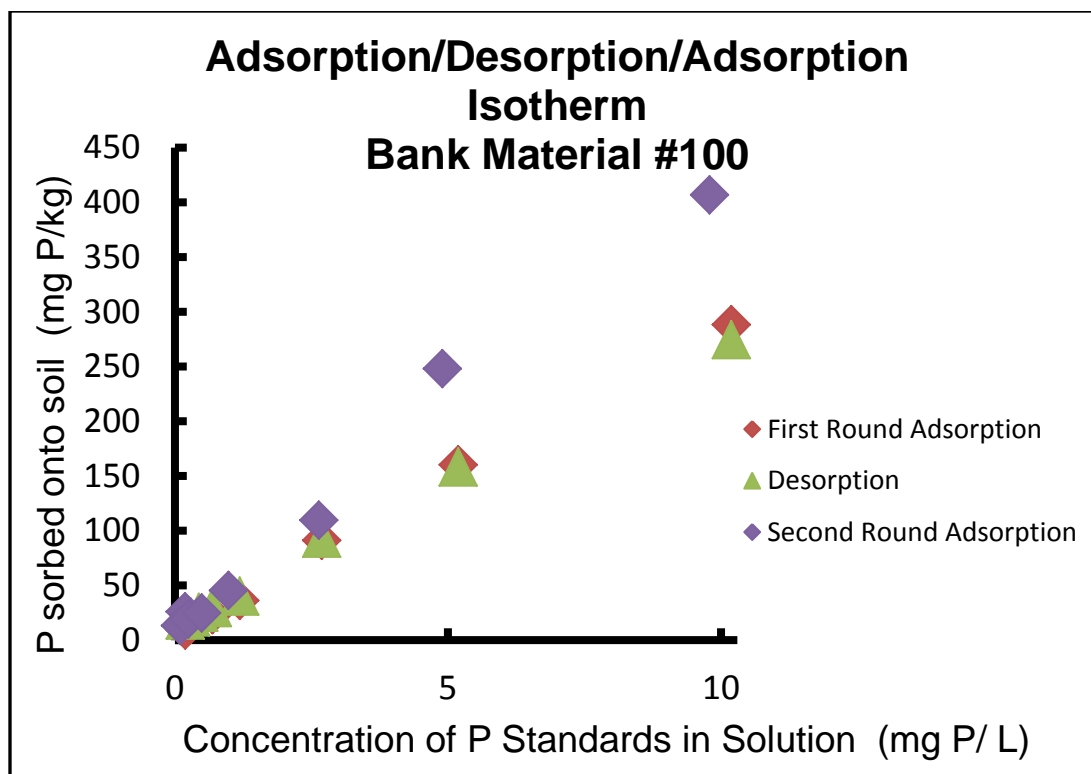


Figure 34. Successive rounds of P adsorption-desorption-adsorption (ADA) test on bank material #100. Although solution P concentration in the second round (desorption) was zero, the desorption data was plotted at the adsorption concentrations to indicate continuity in the ADA tests.

Figure 35 shows the results of the desorption-adsorption-desorption test. Since all the samples were subjected to the same 0.005 M CaCl₂ solution in the first round, there was only one number for all solution concentrations and that is why there are no data points in Fig. 35 for the first round of the desorption test. As expected, the second round of adsorption test showed an increase in P adsorption with an increase in solution P concentration. In the third round of desorption, however, there was very little desorption (Fig. 35-the data points are nearly the same), similar to the ADA test. This again points to the strong binding power of bank material (#100) for P.

Both the ADA and DAD experiments show that the P adsorption process was more active than the desorption process. Furthermore, the chemical make-up of these bank materials

is such that they have a high capacity to adsorb and hold on to the soluble P from solutions or from river waters.

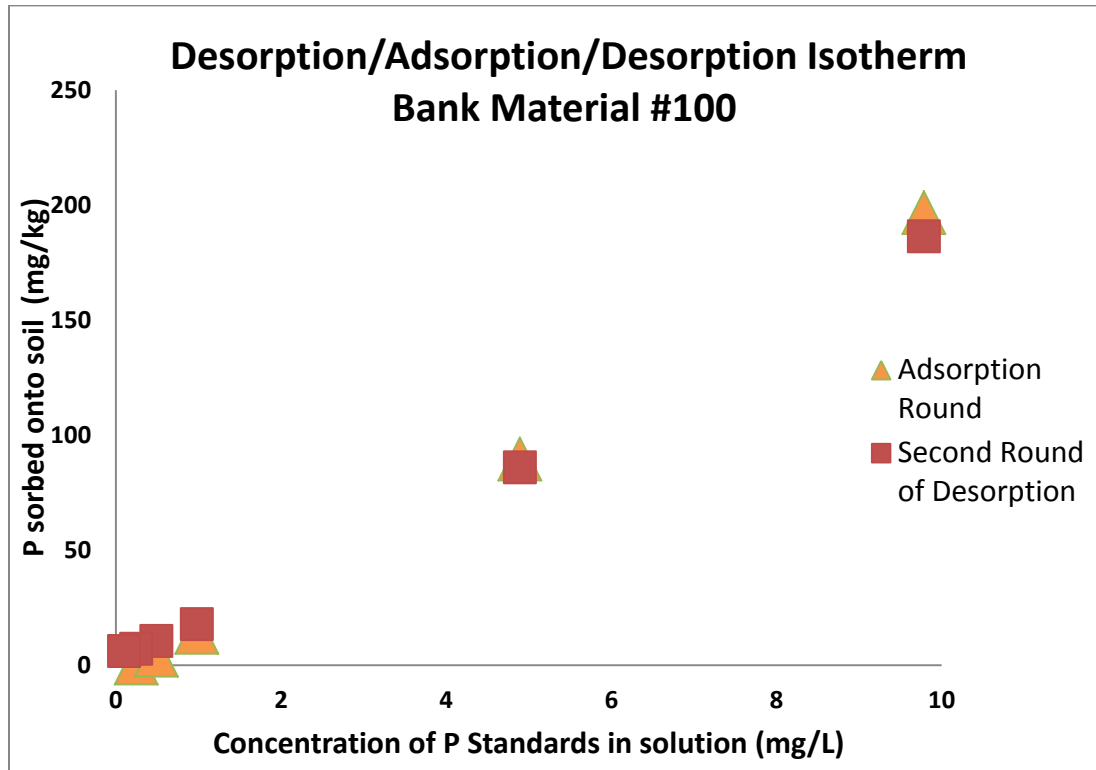


Figure 35. Successive rounds of desorption-adsorption-desorption (DAD) tests on bank material #100. Although solution P concentration in the first and third rounds (desorption) were zero, the desorption data are plotted at the adsorption concentrations to indicate continuity in the DAD tests.

Adsorption Isotherm

Phosphorus adsorption isotherm describes the relationship between the amounts of P adsorbed by the soil as a function of solution P concentration. It is a central soil property in terms of the capacity of a soil to adsorb phosphorus when in contact with a solution (Barrow, 1983). Figure 36 shows the adsorption isotherm of four bank materials (#100, 106, 113, and 128). Adsorption isotherms of other bank materials and surface soils are given in Appendix B Figures B3-B23.

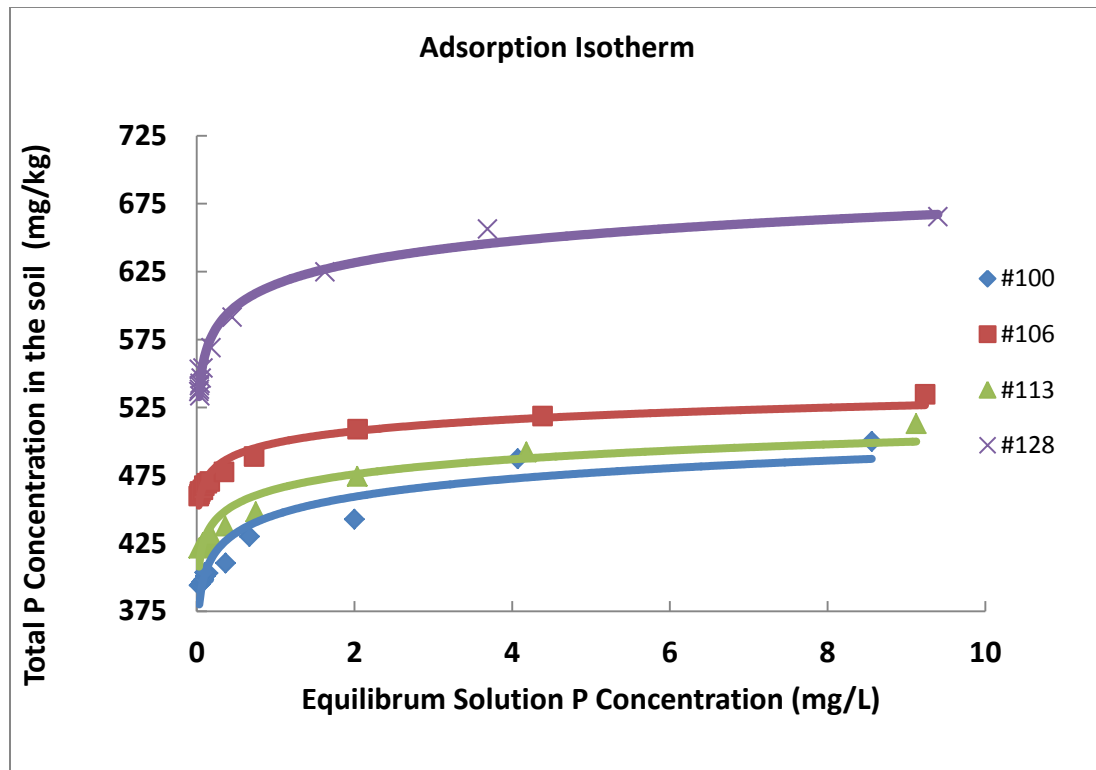


Figure 36. Adsorption Isotherms of four bank materials.

As expected, P adsorption on the bank materials increases with an increase in solution P concentration and then levels off. The leveling off of the adsorption isotherm signals two possibilities, (1) adsorption capacity of the soil has been reached (Brady and Weil, 1999), or (2) there is precipitation of solution phosphorus with calcium desorbed from the soil particles which in turns is limiting the availability of P for additional adsorption. To further evaluate these possibilities, Dr. Paul Bloom ran the Visual MINTEQ program with the chemical analysis of the bank material #100 and the thirteen P concentrations used in our adsorption studies (Paul Bloom, Personal Communication). Visual MINTEQ has the ability to simulate chemical speciation at various concentrations. The key parameter evaluated in the model runs was the saturation index. Positive values of the index indicate over saturation and thus the possibility of solution P precipitation. The simulation results showed that only at the highest initial P concentration of 10 mg/L was there some indication of rapidly forming precipitate of calcium phosphate (CaHPO_4 or $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The model results do not show how much P will be precipitated out of

the solution. Since the mixing solution had a very small concentration of calcium (0.005 M), precipitation at <10 mg/L phosphorus concentration was considered unlikely.

Various formulations have been suggested for representation of P adsorption isotherms such as shown in Fig. 35. Among the most common formulations are the Freundlich (Eq. 2) and the Langmuir (Eq. 3) adsorption isotherm.

$$q = K_f * C^{1/n} \quad [2]$$

$$q = \frac{(S_{max} * K_L * C)}{(1 + K_L * C)} \quad [3]$$

where q is the phosphorus concentration adsorbed on the soil material, C is the equilibrium phosphorus concentration in solution, K_f , $1/n$, S_{max} , and K_L are the best fit parameters that vary with bank material or soil type. S_{max} refers to the maximum adsorption capacity of the soil material.

In Freundlich adsorption isotherm, n values are generally less than 1. When n equals one, the adsorption isotherm reverts to linear adsorption isotherm (Eq. 4). Depending upon the scale of observations, all three adsorption equations could be applied to the laboratory measured adsorption data.

$$q = K_D * C \quad [4]$$

where K_D is the slope of the linear adsorption isotherm.

In Table 21 are summarized the best fit parameters for the Freundlich adsorption isotherm for various materials tested in this study. K_f is the intercept whereas $1/n$ is the slope of the isotherm line. K_f values follows the trend prairie soil > lacustrine bank material > alluvium bank material > agricultural soils > till bank material.

Correspondingly, the slope ($1/n$) of the Freundlich isotherm (binding ability) follows the trend agricultural soils > prairie soils > till bank material > alluvium bank material > lacustrine bank material (Table 21). Some of the differences in K_f and $1/n$ may be due to

unequal sample size. Since one of the agricultural soils had limited adsorption in the range of solution concentrations tested in this study, the data for this soil is not included in the averages shown in Table 21. This sample was taken from a field close to a hog production facility and thus appears to have been regularly fertilized with hog manure. Total P concentration in this soil was 952 mg/kg; a very high value.

In Table 22 are summarized the parameters of the Langmuir adsorption isotherm where K_L is the slope of the isotherm and reflects the P binding strength of the soil, and S_{max} is the maximum potential of the soil material to adsorb P. Individual sample isotherm constants are given in Appendix C Tables C1 and C2. The binding energy (slope, K_L) in the Langmuir adsorption isotherm followed the trends: lacustrine bank material > alluvium material > prairie soils > till bank material > agricultural soils. This means that the bank materials in general have a stronger capacity to hold/retain P after its exposure with solution P. Among the material tested the prairie soils had the maximum capacity for adsorption (S_{max}) followed by lacustrine bank material, agricultural soil, alluvium bank material, and till bank material (Table 22). As mentioned in the results for the Freundlich adsorption isotherm, some of the differences in trends for the Langmuir adsorption isotherm may be due to unequal number of samples among various materials. When interpreting the S_{max} values for various bank materials and soils one must keep in mind that these values are for 24 hour single stage adsorption. With extended equilibration time, a two stage sorption could also develop if the environmental conditions are favorable.

Table 21. Average \pm standard deviation of Freundlich adsorption isotherm constants (K_f and $1/n$) for various bank materials and surface soils.

Materials	Sample Population (N)	K_f , (mg/kg)	$1/n$
Till Bank Materials	9	469 \pm 99.7	.07 \pm .03
Alluvium Bank Materials	3	521.3 \pm 114.7	.06 \pm .03
Lacustrine Bank Materials	3	558.3 \pm 106.3	.05 \pm .02
Surface Prairie Soils	4	598 \pm 151.2	.08 \pm .03
Surface Agricultural Soils	2	491 \pm 50.9	.08 \pm .00

Table 22. Average \pm standard deviation of Langmuir adsorption isotherm constants (K_L , S_{max}) for various bank materials and surface soils.

Materials	Sample Population (N)	K_L (L/mg)	S_{max} (mg/kg)
Till Bank Materials	9	51.7 ± 26.5	483.8 ± 90.6
Alluvium Bank Materials	3	62.7 ± 84.9	563.0 ± 77.6
Lacustrine Bank Materials	3	106.7 ± 72.5	581.7 ± 121.2
Surface Prairie Soils	4	54.5 ± 65	645.0 ± 139.1
Surface Agricultural Soils	2	7.0 ± 1.4	575.5 ± 70.0

Equilibrium Phosphorus Concentration (EPC_0)

As stated earlier, equilibrium phosphorus concentration (EPC_0) refers to the P concentration in solution above which soil or sediment particles adsorb P and below which they desorb P. As several measurements were taken at P concentrations less than 1 mg/L, EPC_0 was estimated using the linear fit to that adsorption data. Figure 37 shows an example on the determination of EPC_0 for bank material #100 using the adsorption data for equilibrium phosphorus solution concentrations less than 0.2 mg/L. In this sample, the best fit line shows an EPC_0 of 0.076 mg/L. The EPC_0 value of 0.076 mg/L indicates that this sample will adsorb P from the solution or the river water if the SRP concentration is greater than 0.076 mg/L.

In addition to the linear fit of the adsorption data for solution concentration <0.2 mg/L, we also estimated the EPC_0 using the Langmuir adsorption isotherm (Fang et al., 2002). Table 23 summarizes the EPC_0 values for various materials tested using both the linear and the Langmuir adsorption isotherms. Bank material EPC_0 values with both analyses follow the trend: alluvium materials $>$ lacustrine materials $>$ till materials (Table 23). EPC_0 values of various bank materials are within the range of EPC_0 values reported by James et al. (2002), James and Barko, (2004), and James and Larson (2008) for sediments from the

Redwood River (0.074 mg/L), the Minnesota River (0.117 mg/L), and Lake Pepin (0.155 mg/L), respectively. Among the banks materials and surface soils, EPC_0 follow the trend: agricultural soils > prairie soils > bank materials. With the exception of soil T, the EPC_0 values of all agricultural soils measured in this study were similar to the values reported by Fang et al. (2002). EPC_0 of soil T was higher because of apparent regular hog manure application. A plot of EPC_0 values vs. silt plus clay content of various materials tested in this study showed no definitive relationship between these variables (Fig. 38).

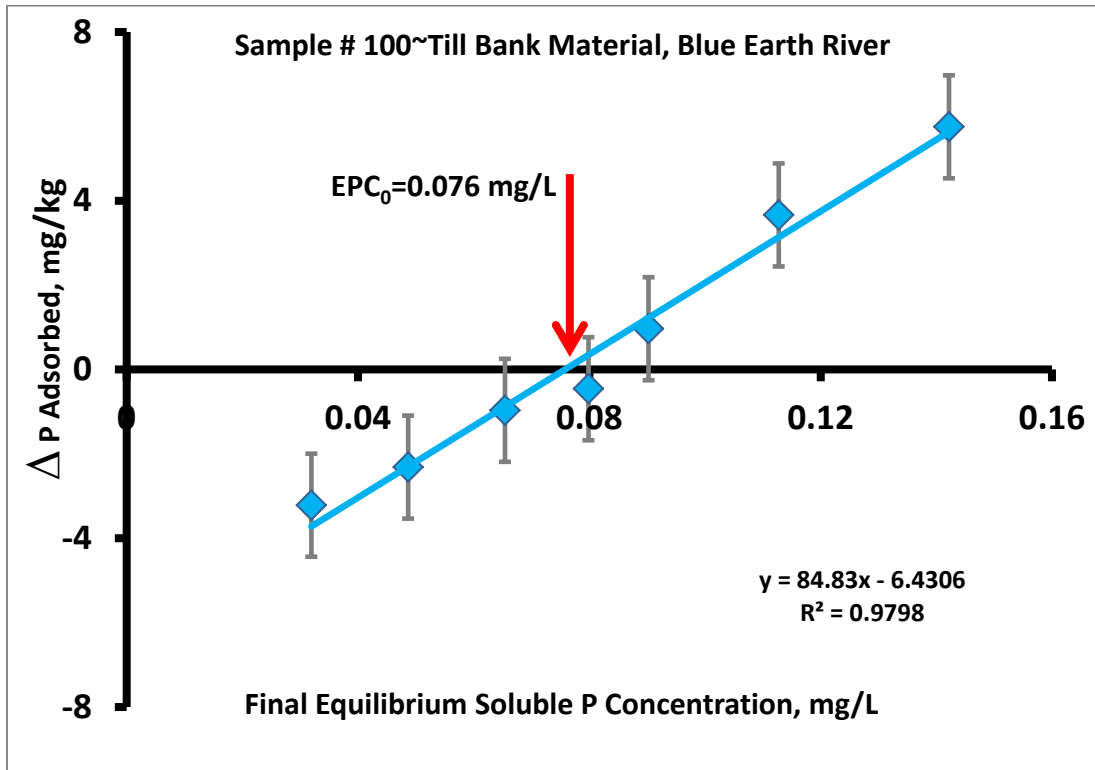


Figure 37. Linear adsorption isotherm at low concentrations (<2 mg/L) for bank material #100.

Table 23. Average \pm standard deviation of EPC₀ values obtained for various bank materials and surface soils using the best fit linear adsorption for solution P concentration <0.2 mg/L and from the Langmuir adsorption isotherm. Bank materials are broken down by parent material type whereas surface soils are grouped into prairie and agricultural soils. Since EPC₀ of the alluvium materials was a bit higher, a median EPC₀ value for the bank materials is also included.

Materials	Linear Isotherm EPC ₀ Value (mg/L)	Langmuir Isotherm EPC ₀ Value (mg/L)
	Average \pm Standard Deviation	
Till Bank Materials	.07 \pm .04	0.12 \pm .06
Alluvium Bank Materials	0.42 \pm .34	0.52 \pm .52
Lacustrine Bank Materials	0.16 \pm .12	0.15 \pm .15
Prairie Soils	0.17 \pm .10	0.2 \pm .16
Agricultural Soils	2.66 \pm 3.67	0.86 \pm .25
Median Value for bank materials	0.07	.16

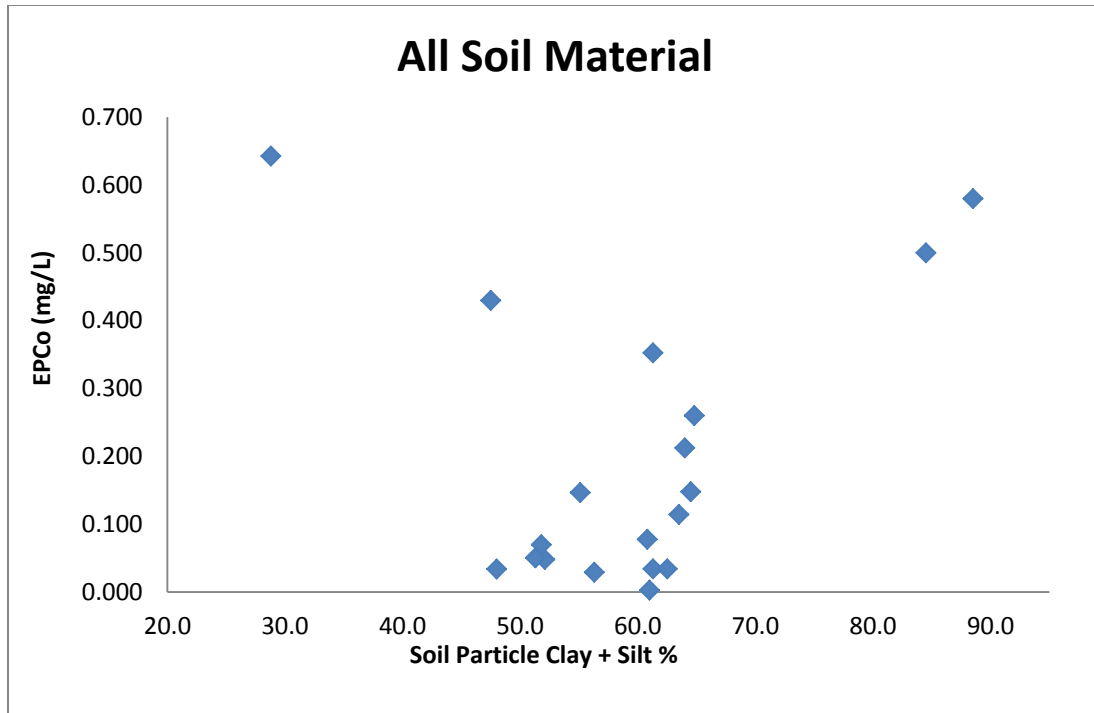


Figure 38. Relationship between EPC_0 values and the clay+ silt % of various soil materials (bank materials and surface soils) tested in this study.

TP Distribution with Depth

The bank materials tested in the adsorption studies were gathered randomly from easily accessible banks. Record was not made of the depth from which these samples were taken. Because of high TP content of these materials, a question came up as to representativeness of the TP content of these samples for the basin and whether TP content of bank materials at deeper depths is nearly similar. This information was deemed important considering many of the sloughing river banks in the Greater Blue Earth River Basin are tall and are not readily accessible for sampling. This question is similar to the question that was raised in bank erosion study of Kessler et al. (2012) on variation in bulk density with soil depth. To address the above question, we supplemented our samples with samples from archived deeper cores taken by the Minnesota Geological Survey in Blue Earth County (Fig. 24). These cores are now stored in the Minnesota Department of Natural Resource facility in Hibbing, MN. Bulk densities of the samples with depth for all five cores are shown in Fig. 39. Because of the expense of analyzing all samples from

all five cores, TP, and particle size analysis was done only on one core (SC-8). A total of 55 samples representing a depth of 69 meters were collected from this archived core. Since this core was located in the Le Sueur River watershed, it was presumed to be representative of the buried material in that watershed.

In general, there is an increase in bulk density with soil depth at all five locations in Blue Earth County (Fig. 39). Specifically in core SC-8, the bulk density averaged around 1.8 Mg/m³ in the top 20 m, 2.2 Mg/m³ in 30-40 m depth, and then around 1.9 Mg/m³ in 70-90 m depth (Fig. 39). Over the whole core depth, the bulk density averaged at 1.91 Mg/m³.

On these cores, the particle size analysis was done by the University of Wisconsin Soil Testing Laboratory, Madison, WI and the TP analysis was done by the University of Minnesota Soil Testing Laboratory, St. Paul, MN. Data on soil texture, bulk density and TP are given in Appendix D, Figures D1 and Table D1. Although the samples in this core had a wide range of textures, sandy loam and loam were the predominant soil textures.

Average Bulk Density in Deep Soil Cores

Bulk Density (Mg/m^3)

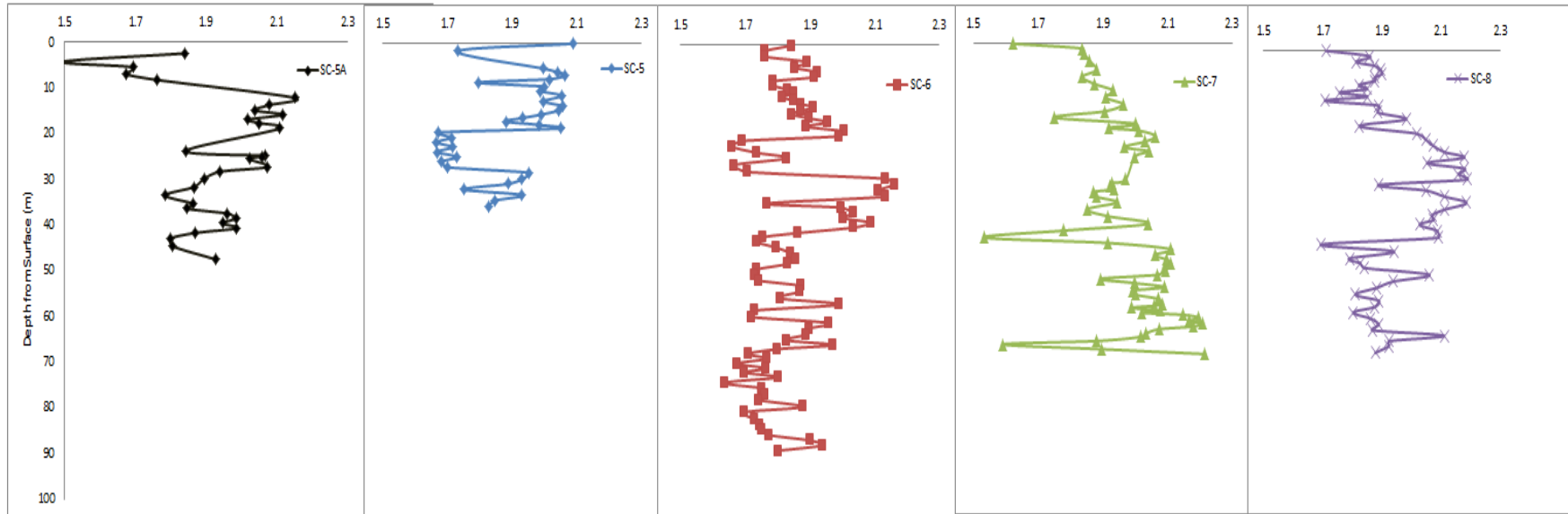


Figure 39. Distribution of bulk density with depth for 5 deep soil core samples taken by the Minnesota Geological Survey in Blue Earth County. Each point is an average of three measurements.

Total P content of bank materials in core #8 ranged from 116 mg/kg to 936 mg/kg, with the maximum TP concentrations occurring at the deepest depths (Fig. 40). For this core, the TP content of samples averaged at 470 mg/kg. A comparison of TP concentration of the randomly collected samples used in the adsorption studies with samples in this core shows that the TP content of the samples used in the adsorption studies are representative of the samples at various depths in this core.

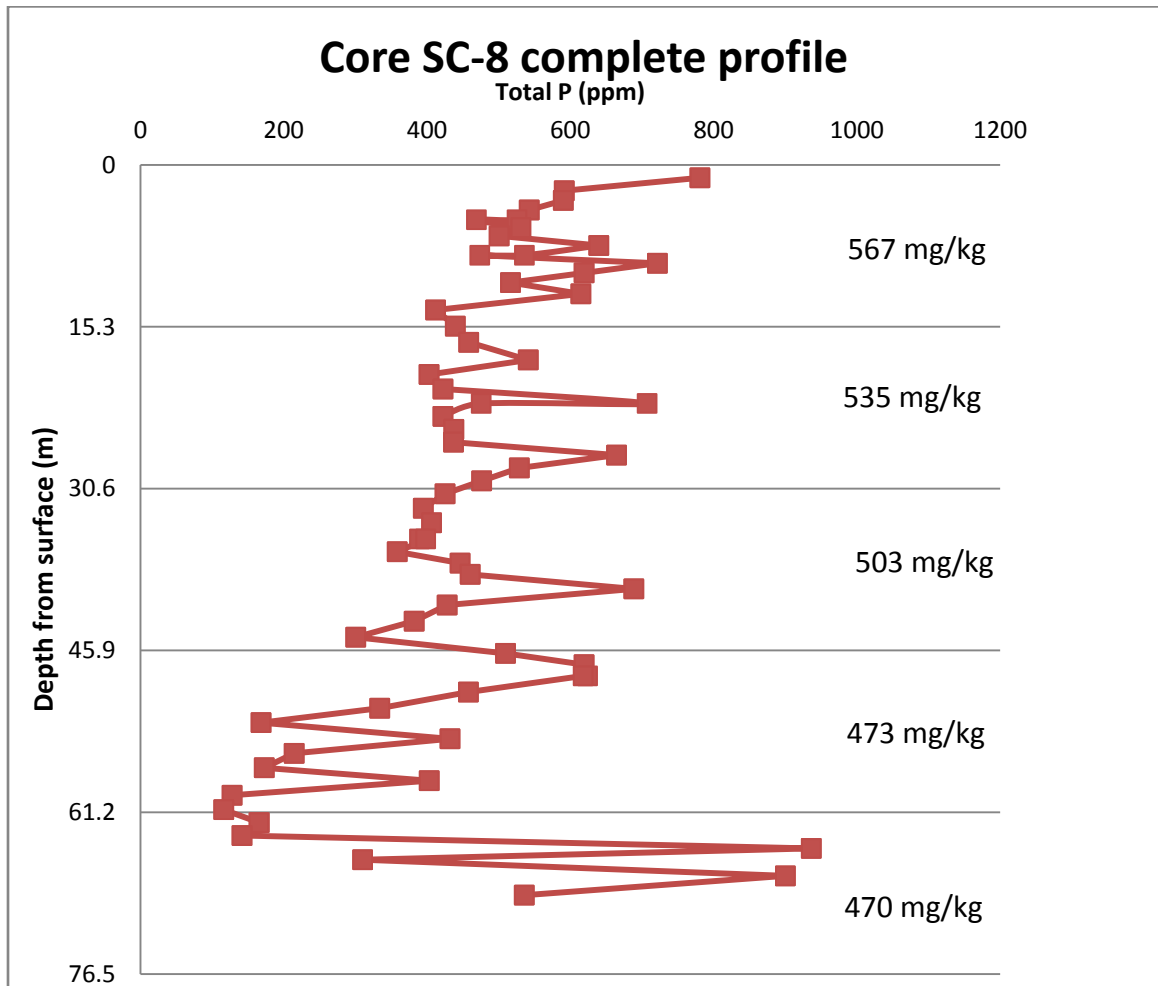


Figure 40. Variation in soil total P (TP) with depth for core SC-8. The numbers on the right correspond to depth weighted TP (mg/kg) concentrations at 15.3 m increments.

Soil P Fractionation

The next objective of this research was to assess (1) the distribution of different P fractions in various bank materials, surface prairie soils, and surface agricultural soils, and (2) how those distributions compare with distribution of P fractions in Lake Pepin sediments. The P fractions characterized in bank materials, prairie soils, and agricultural soils are calcium-P, aluminum-P, iron-P, Labile organic-P, refractory organic-P, and loose-P.

In figures 41- 44 are shown the average distribution of P fractions in various materials by land use (till materials, prairie soils, agricultural soils, and the Minnesota River sediments). Minnesota River sediment values were taken from James and Larson (2008). It appears that for each material type there is a predominant P fraction. For examples, within the till bank materials, calcium bound P dominates followed by loose P, iron bound P, aluminum bound P, and then labile P (Fig. 41). On the other hand, the prairie soils contain high levels of refractory organic P followed by labile organic P, calcium bound P, and then aluminum bound P (Fig. 42). High levels of organically bound P in prairie surface soil is not surprising considering the high levels of organic matter (LOI) found in these soils. Figure 42 is composed primarily of restored prairies of varying time frame; however it does contain a sample (sample L) from “virgin prairie” collected at Jeffers Petroglyphs in Brown County. Most of the organic P in surface prairie soils will be from deeper depths as the plants adsorbed nutrient through roots and then recycle them after senesce. Interestingly, the Petroglyphs soil is dominated by organic P, but of the labile variety (with 50% labile and 22% refractory). Comparatively, the refractory organic P dominated (41%) the restored prairie soils.

Within the surface agricultural soils, there are two distinct groups of P fractions: nearly uniform distribution of calcium bound P, aluminum bound P, and refractory organic P; and nearly uniform distribution of iron bound P, labile organic P, and loosely bound P (Fig. 43). James and Larson (2008) had reported the P fraction analysis in the Minnesota River sediments taken 10 miles upstream of the confluence with the Mississippi River in St. Paul. Their results show a similar distribution of P fractions compared to agricultural surface soils, in that 50% of the P is bound in labile forms and the remaining 50% is in refractory

forms (Fig. 44). However, their sediments are a repository of all upstream influences and contained fine particle from all sources; bank materials, agricultural soils, and urban soils. Moreover P fraction analysis in our samples (bank materials, surface prairie, and surface agricultural soils) includes P content of the sand fraction. It is likely that sand content from upstream locations were minimal or absent, in James and Larson (2008) river sediments, both due to settling as well as due to dredging. Some of the differences in P fraction distribution between bank materials, surface soil and river sediments may be due to differences in number of samples for each population type.

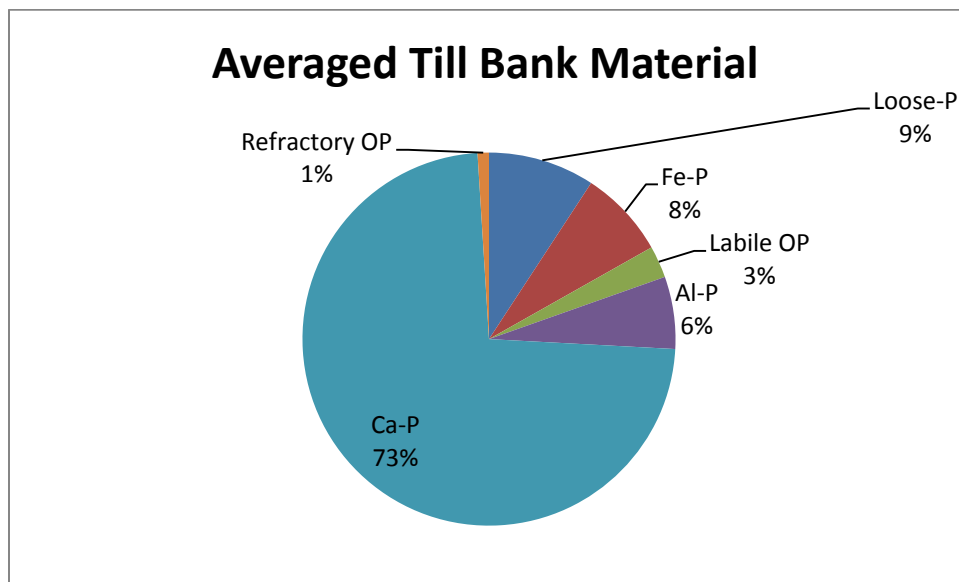


Figure 41. Distribution of P fractions in till river banks from Blue Earth County. The values are averages over all till samples (# 100, 106, 116, 122, 123, 130, 131, and 135) tested in this study.

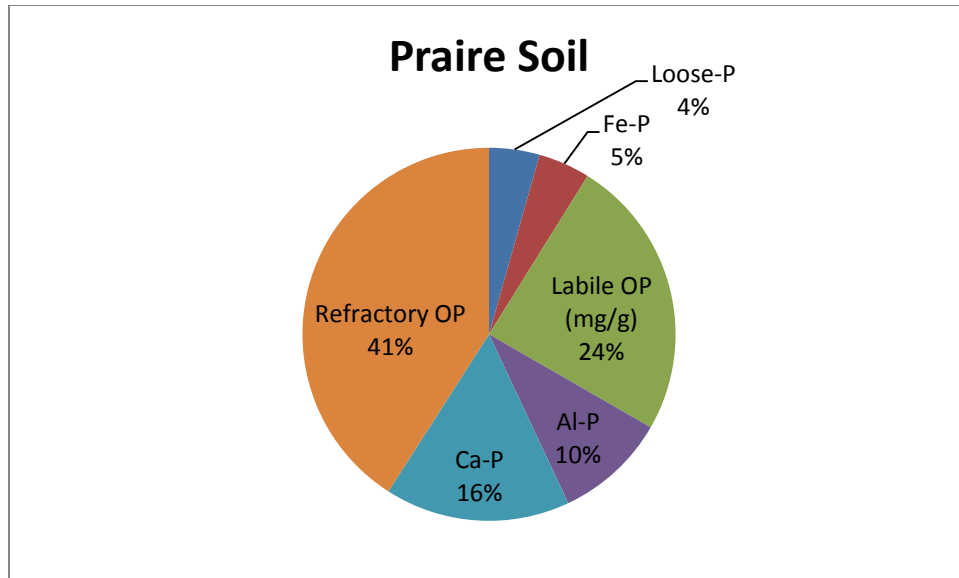


Figure 42. Distribution of P fractions in surface prairie soil averaged over all prairie samples (# B, C, D, G, J, and L) tested in this study. Prairie samples were collected from various locations in the Minnesota River Basin.

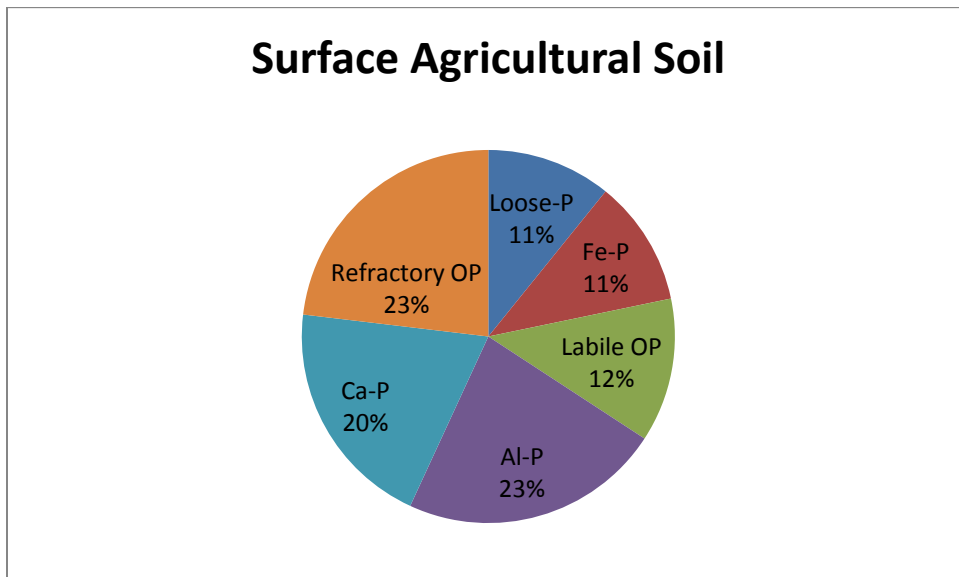


Figure 43. Distribution of P fractions in surface agricultural soils. The values are averages over two samples taken in Blue Earth County (# T and U).

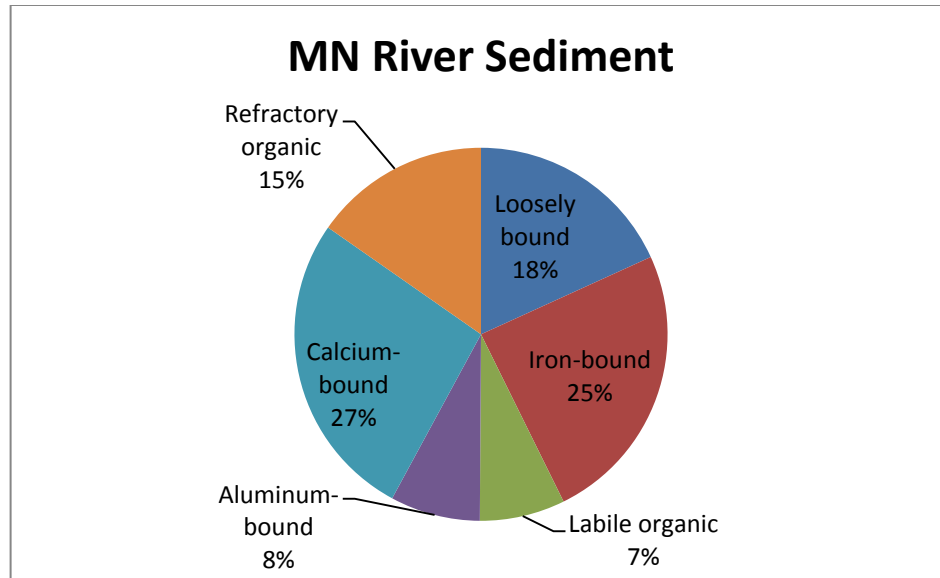


Figure 44. Distribution of P fractions in one sample of the Minnesota River sediments above its confluence with the Mississippi River (after James and Larson, 2008).

We also compared P distribution in our bank materials and surface soils with those of Lake Pepin sediments reported by Engstrom et al. (2009). Since the procedures used in this study are slightly different than the procedures used by Engstrom et al. (2009) in Lake Pepin P fractionation, we combined the six fractions in our study to match the three fractions reported by Engstrom et al. (2009). Comparatively, the procedure used by Engstrom et al. (2009) followed the procedures of Hietjjes and Lijklema (1980) and Plumb (1981). In this procedure P is fractionated into NaOH-P, HCl-P, and residual-P. Since NaOH was the first fraction in Engstrom's et al. (2009) analysis, we assumed this to be equivalent to iron and aluminum bound P. The HCl extracted P was straight forward calcium bound P and the residual P was assumed to be organic P.

Figures 45- 49 show the comparisons of various P fractions in bank materials, surface prairie and agricultural soils, and the Minnesota River sediment relative to Lake Pepin sediments. The dominant fraction in banks materials and prairie soils is calcium bound P and organic P, respectively. Comparatively, aluminum/iron bound P, calcium bound P and organic P are nearly equally distributed in the agricultural soil. Within the Minnesota River sediment there is also nearly even distribution between these three fractions with a slight preference towards organic P. The strong calcium fraction in the Minnesota River sediment

may be buffered by the bank material calcium levels. Lake Pepin sediment showed the dominance of aluminum/iron bound P with near equal distribution between organic and calcium bound P.

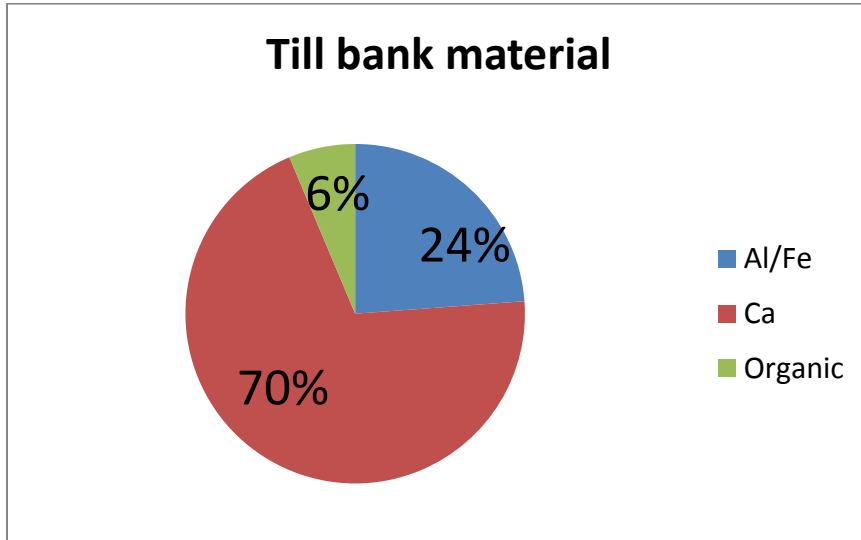


Figure 45. Distribution of P fractions in various bank materials. These P fractions are equivalent to fractions characterized using the procedures of Hieltjes and Lijklema (1980) and Plumb (1981) as reported by Engstrom et al. (2009) for Lake Pepin sediments.

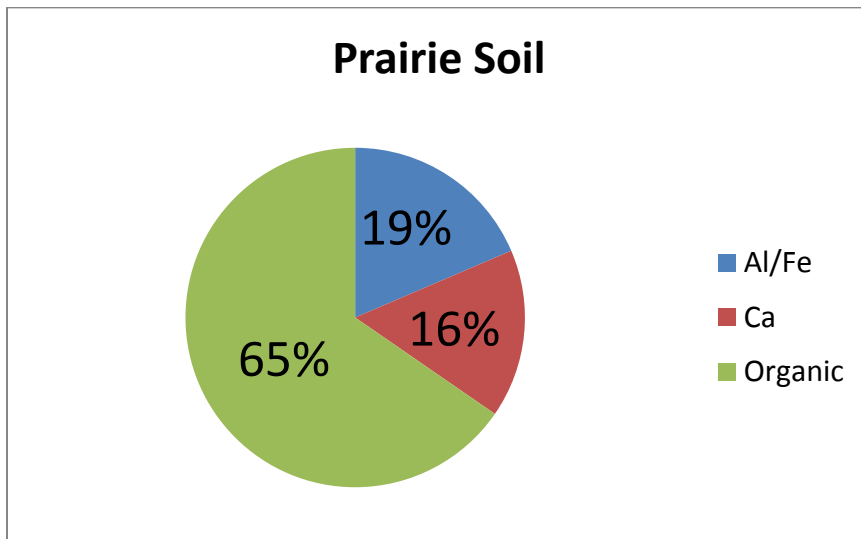


Figure 46. Distribution of P fractions in surface prairie soils. These P fractions are equivalent to fractions characterized using the procedures of Hieltjes and Lijklema (1980) and Plumb (1981) as reported by Engstrom et al. (2009) for Lake Pepin sediments.

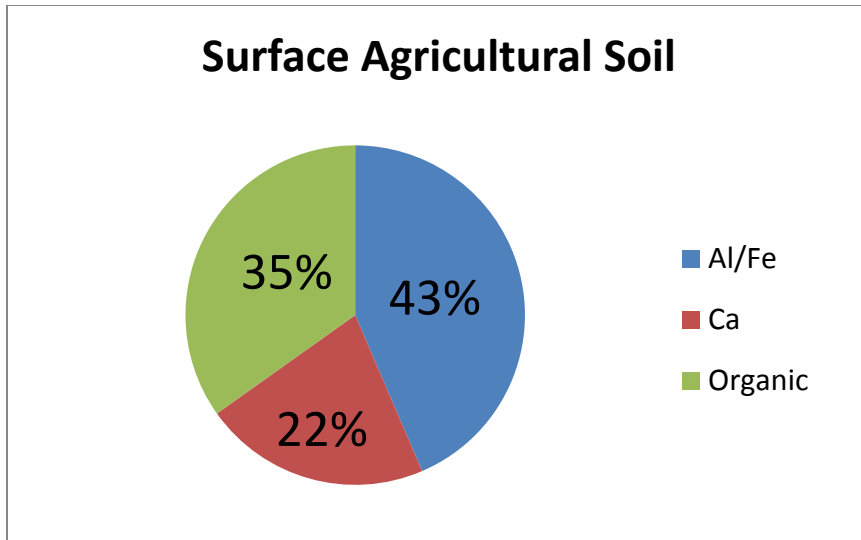


Figure 47. Distribution of P fractions in surface agricultural soils. These P fractions are equivalent to fractions characterized using the procedures of Hieltjes and Lijklema (1980) and Plumb (1981) as reported by Engstrom et al. (2009) for Lake Pepin sediments.

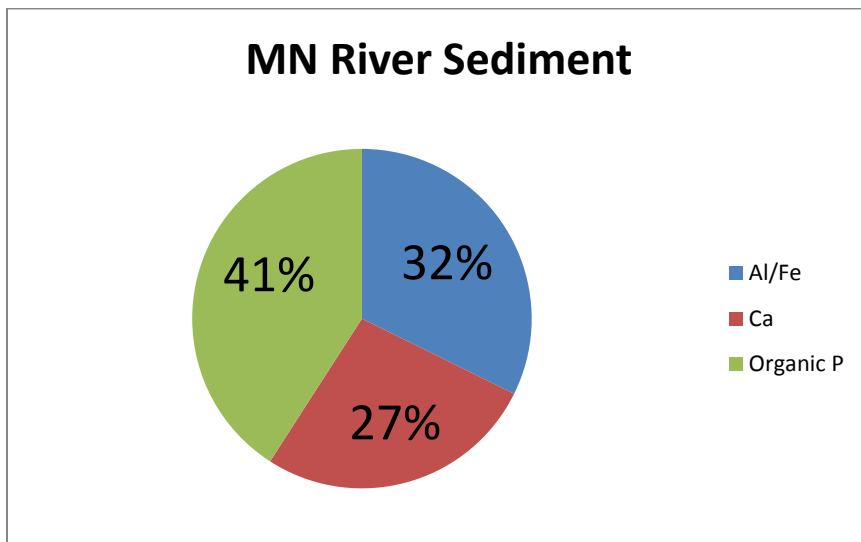


Figure 48. Distribution of P fractions in the Minnesota River sediments 10 miles upstream of its confluence with the Mississippi River (after James and Larson, 2008). These P fractions are equivalent to fractions characterized using the procedures of Hieltjes and Lijklema (1980) and Plumb (1981) as reported by Engstrom et al. (2009) for Lake Pepin sediments.

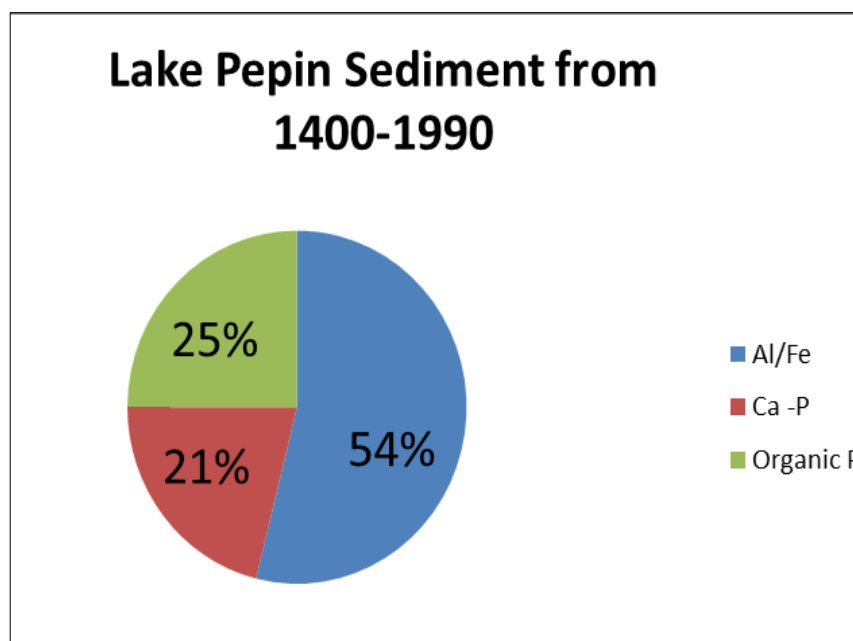


Figure 49. Distribution of various P fractions in Lake Pepin Sediments as reported by Engstrom et al. (2009) using the procedures of Hieltjes and Lijklema (1980) and Plumb (1981).

Some of the differences in P fraction distribution between various sources and sediment samples in Lake Pepin are likely due to (1) differences in techniques in P fraction characterization between this study and Engstrom et al. (2009) study, and (2) due to physical (particle enrichment) and chemical (P adsorption) interactions that bank and surface soil particles may undergo during their transport to downstream locations.

However, the variation in distribution of P fractions in the Minnesota River and Lake Pepin sediments relative to various source materials raises two overarching questions: (1) how are P fractions distributed in different size particles of various source materials in the Minnesota River Basin? and (2) what might be the contributions of these particles to the Minnesota River and Lake Pepin sediments? The second question deals with the enrichment of various size particles from different source materials. Further research is needed to address both these questions.

Effect of Particle Size on Total P

Several studies have shown that TP concentration increases with decreasing particle size (Day et al., 1987; Agbenin and Tiessen, 1995; Sinaj et al., 1997). Recently, James (2010) showed a similar trend in the Minnesota River sediment with a four times higher P holding capacity in clay particles relative to sand particles. We applied this question to our bank materials in terms of particle size and TP content. Results of the TP analysis for three particles fractions for till bank material #100 are shown in Table 24. Total P concentration in our sand fraction (>50mm) was slightly less than (165 mg/kg) the value measured by James (2010) for the >63mm particles in the Minnesota River sediment (265 mg/kg).

Relative ratios of TP for sand, silt, and clay fractions in the till material #100 was 1, 2.32, and 3.65, respectively. These are slightly different than the values reported by James (2010) for six fractions (Table 3). The relative ratios of TP in James (2010) study were 1.0, 1.5, 1.9, 2.0, 3.0, and 4.1 for particles of >63 μm , 31.2-63.0 μm , 15.6-31.2 μm , 7.8-15.6 μm , 3.9-7.8 μm , and <3.95 μm diameter, respectively. These differences between the bank material in our study and suspended sediments in James (2010) study may be due to (1) differences in particle size scales between the two studies, (2) one till material compared to James (2010) integrated sediment sample from many sources including different bank materials, agricultural soils, and urban soils, and (3) the difference in TP between the two samples, in that soil #100 has a TP of 397, and James (2010) sample was over 930 mg/kg. In our study, we used USDA classification scheme for various particle size fractions.

Table 24. Total P (TP) analysis and its relative ratios for three particle sizes of till material #100.

Particle Diameter (μm)	TP (mg/kg)	Relative Ratios
>50-2000 (Sand)	165	1.00
2-50 (Silt)	384	2.32
<2 (Clay)	603	3.65

Factors Affecting P Concentration in Lake Pepin Sediments

This section discusses factors that possibly explain the increases in inorganic P or TP concentration in Lake Pepin sediments over time. Using two cores at each of the five transects in Lake Pepin, Engstrom et al. (2009) showed that TP concentration in sediment increased over time since the European settlement. However, most of this increase in TP concentration was in the NaOH fraction P (iron and aluminum bound P); HCl extracted P and residual P were relatively constant over time. The continuous increase in NaOH extracted P (Fig. 8) was an indication of possible P adsorption by sediments in the river system. In general, NaOH extracted P in lake sediments varied from 280-500 mg/kg from 1400-1850 AD and these concentrations increased over time to an average (over 2 replications along 5 transects) value of 1030 mg/kg between 1950-1970 AD.

Since our bank materials were high in calcium bound P (HCl extracted P) and since our adsorption tests were also with respect to inorganic P adsorption, we focus the discussion on factors controlling P in Lake Pepin sediment only in terms of inorganic P. The other reasons for inorganic P comparisons rather than the TP comparisons in this section are (1) the relative constant organic P concentrations in Lake Pepin sediments over time and (2) the uncertainty in the origin of organic P sources (algae, surface soils, river pollution) between the pre-settlement and the post settlement times.

In general, inorganic P (NaOH extracted P and HCl extracted P) concentration were in the range of 500-700 mg/kg from 1400-1850 AD and these concentrations increased to an average (over 2 replications along 5 transects) value of about 1300 mg/kg between 1950 and 1970 AD. The inorganic P values of our bank materials were calculated by subtracting the organic P values from TP concentrations. Organic P content of the bank materials was taken from our sequential extraction analysis.

Pre-Settlement Times:

Since there were no anthropogenic source of P to the rivers prior to pre-settlement times (<1850), this section assesses if river bank sediments in the Minnesota River basin can explain the inorganic P concentration in Lake Pepin sediments prior to 1850 (prior to European settlement).

The first factor in this analysis was hypothesized to be the enrichment of sediment derived from bank materials. Sediment enrichment refers to the sorting of the particles where heavier particles with lower phosphorus concentrations are left behind in the basin (in the form of sand bars), and finer particles with higher phosphorus concentrations are transported downstream to locations such as Lake Pepin (Sharpley, 1985; James, 2010). In other words, there are higher amounts of P present in smaller amounts of sediment. This increase is calculated by using the concept of Enrichment Ratio defined as the amount of all particles in a soil material to the amount of particles carried downstream. For our first set of calculations, we assumed that all sand particles of bank materials and surface prairie and agricultural soils are settling in upstream of Lake Pepin and only silt and clay particles are finding their way to Lake Pepin (Eq. 5).

$$\text{Enrichment Ratio (ER)} = \frac{100}{\text{silt \%} + \text{clay \%}} \quad [5]$$

In Figure 50 are shown the comparisons of average ER values among various bank materials, surface prairie and agricultural soils, and samples from soil core SC-8. For all materials, ER varies from 1.00 to 14.3 with a median value of 2.1. The till and lacustrine bank materials have a narrow range of ER values compared to alluvium bank materials. Between the 1st and 3rd quadrants, the interquartile range (IQR) in ER values is less than 0.5 for the till and lacustrine bank materials. Comparatively for the alluvium bank material, ER ranges from 1.9-5.2 and has an IQR of 1.2. Total range in ER values for the surface prairie soils is from 1.4-2.8, with half of the values clustered below 1.6. The enrichment ratios for the agricultural soils are highly clustered, which may be the result of agricultural activities or due to the limited sampling population. The particle enrichment ratio of samples at various depths in deep soil core SC-8 varies from 1.2 to 14.3, with a median

value of 2.4. Despite the strong outlier values in deep core soil samples, the average ER values are representative of the ER values of bank materials in random sampling.

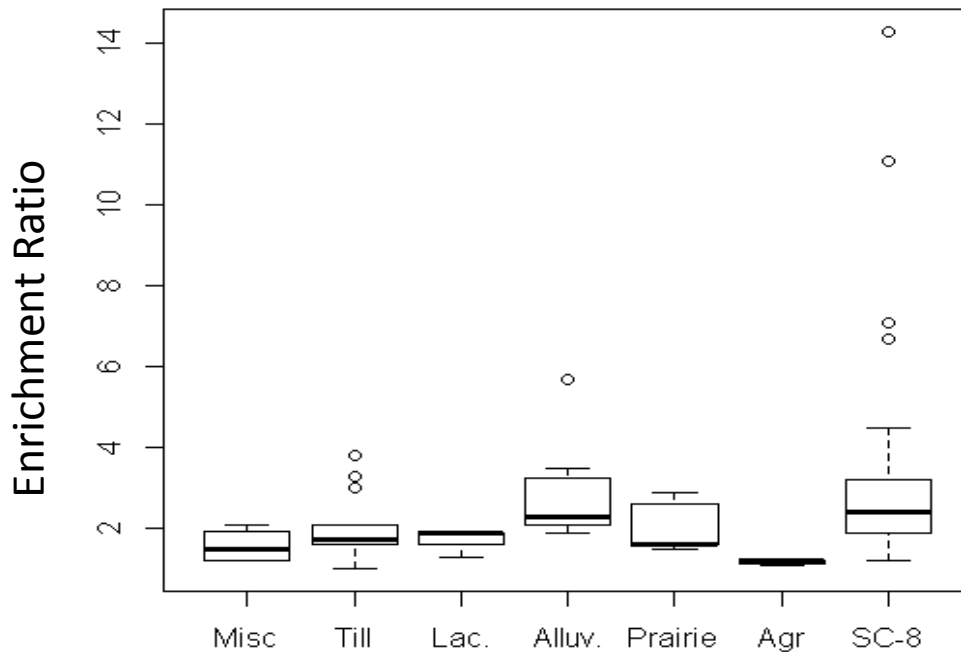


Figure 50. Comparisons of enrichment ratios (ER) among various river bank materials, surface prairie and agricultural soils, and samples from soil core 8 (SC-8) taken by the Minnesota Geological Survey in Blue Earth County.

The particle enriched inorganic P value for the Lake Pepin sediment in the period prior to 1850 was calculated by first removing the organically bound P (OP) and the P associated with the sand fraction. This value was then multiplied with the enrichment ratio (ER) to calculate new inorganic P in sediments. Inorganic P associated with the sand fraction was estimated from the P analysis of dredged material samples taken from the Minnesota River as well as a sample from a sand bar on the Le Sueur River. Arneman (1950) showed that there is higher percent apatite at deeper depths than shallow depths. Lower apatite content at shallow depths was due to dissolution and leaching over time. Arneman (1950) also reported that in C horizon of three main Minnesota soils in Southern Minnesota (Clarion, Nicollet, and Webster), as much as 10% of the heavy minerals in very fine sand fraction were apatite. This possibly explains higher TP content of sands at deeper depths in deep

core SC#8. Based upon our compiled data for the dredge material and the sand bar samples, the average TP was 180 mg/kg with average particle size distribution of 96% sand, 2% silt, and 2% clay. We used this value in our calculations for estimating inorganic P in enriched sediments of bank materials.

$$\text{Particle Enriched inorganic P} = (\text{Total P in the bank material} - 180\text{mg P/kg of sand fraction-organic P}) \times ER$$

In Table 25 are listed the inorganic P, particle size distribution, enrichment ratio, and particle enriched inorganic P of three till bank materials. Particle enriched inorganic P data show that if only silt and clay reach Lake Pepin, particle enrichment will increase the inorganic P concentrations from 397- 462 mg/kg in bank materials to 500- 630 mg/kg in lake sediments. If all the bank material samples from the various parent materials tested in this study undergo this enrichment, the range of particle enriched inorganic P concentrations widens to 383-3600 mg/kg. Particle enriched inorganic P concentrations of all the till bank materials are comparable to the inorganic P concentration in Lake Pepin sediments reported by Engstrom et al. (2009) for the period prior to 1850. This suggests that it is likely that particle enrichment of the river bank materials in pre-settlement times contributed to higher inorganic P of the Lake Pepin sediments. A complete list of all till bank samples enrichment ratios and the particle enriched inorganic P is given in Appendix E Table E1. In these calculations it was assumed that organic matter content of samples was 1% (average for the till samples was $0.9 \pm 0.38\%$), and the organic P concentration was 26 mg/kg (average for the till samples as 26 ± 20 mg/kg).

Table 25. Calculations of particle enriched inorganic P for three till bank materials.

Bank Material ID#	Total P mg/kg	Sand %	Silt %	Clay %	Inorganic P with organic P and sand P removed	Particle ER	Particle Enriched Inorganic P on clay/silt (mg/kg)
100	397	39	33	28	304	1.64	500
106	462	48	30	22	327	1.92	630
130	461	37	33	30	388	1.60	620

In Figure 51 are shown the particle enriched inorganic P distribution of samples from deep core SC-8. In this analysis, it was assumed that organic matter content of samples was 1%, and the organic P concentration was 26 mg/kg. For the 70 meters core depth, particle enriched inorganic P varied from 70-5360 mg/kg with an average concentration of 860 mg/kg. Within the top 30 meters, particle enriched inorganic P varied from 638-1520 mg/kg with an average concentration of 890 mg/kg. These values are generally higher than the particle enriched inorganic P values of random bank material samples described earlier. There is also a distinct difference between the ranges depending upon the depth of the core. This is mainly because deeper core samples have a slightly higher sand percentage and thus greater potential for higher enrichment ratios during transport. Since currently the river banks are about 30 meter tall, the data from deeper depth (70 m) for core SC-8 may not be relevant. However, if tributaries keep on eroding at their base, banks will eventually become taller and then the deeper values will become relevant. The materials seen around 60 meter depth are primarily composed of sand and thus have a very low capacity to hold P. Below this layer is a sandy loam layer that has high TP. It is this layer that gives a very high inorganic P for enriched particles and skews the data into the 5000 mg/kg range. However, comparison of the enriched inorganic P from core samples provides additional evidence that the enrichment of bank materials adequately explains the pre-settlement inorganic P of Lake Pepin sediments.

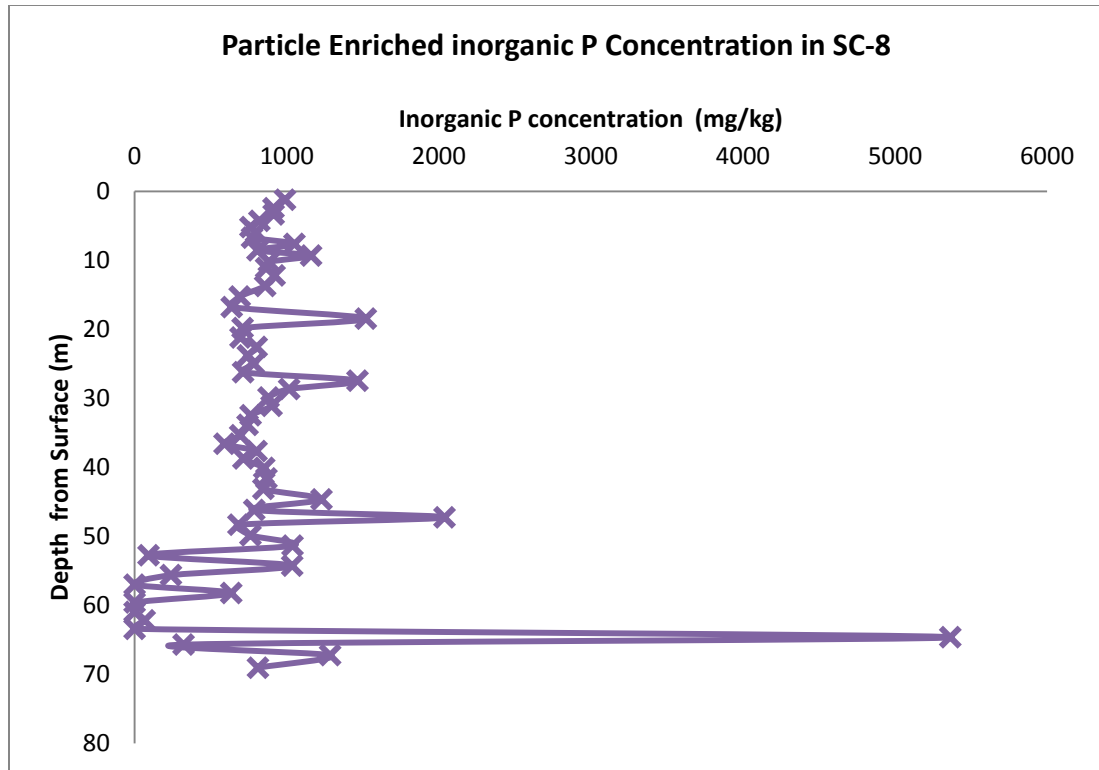


Figure 51. Distribution of particle enriched inorganic P concentrations in deep core SC-8. It was assumed that organic matter content was 1%, and organic P 26 mg/kg.

Post-Settlement times: In an earlier chapter, we outlined historical records that describe various factors that may have influenced phosphorus concentration in the Minnesota River and the Mississippi River upstream of Lake Pepin. These factors included dumping of 500 tons of garbage everyday by each of the Twin cities of Minneapolis and St. Paul, dumping of waste from the South St. Paul stockyard, dumping of high P waste water by industry especially the food industry, discharge of high P waste water from various sewage treatment plants, and use of high P in household detergent. The FWPCA (1966) reported that TP concentration of wastewater from Pig Eye STP varied between 1.2 to 7.3 mg/L with an average of 4.41 mg/L. In this section, we present a sensitivity analysis that shows how P adsorption from river waters along with particle enrichment affects inorganic P concentration of sediments from bank materials. We ran this sensitivity analysis at dissolved P concentrations of 0.5, 1.0, 2.0 and 3.0 mg P/L of river water (Table 26-29). These calculations are done after adjustment for organic bound P and P content of sands. Although the higher P concentrations in this sensitivity test are more representative of

effluent concentrations and these concentrations will be diluted when wastewater mixes with river water, there could be some short period of time (near the outfall) when sediment may come in contact with the wastewater at near original P concentrations discharged from the STP.

The results of the above sensitivity analysis show that inorganic P concentrations of lake sediment derived from three till materials listed in Tables 26, 27, 28 and 29 will vary from 523-718 mg/kg; 548-816 mg/kg; 586-997 mg/kg; and 616-1166 mg/kg for river water P concentration of 0.5, 1.0, 2.0, and 3.0 mg/L, respectively. In general, these concentrations are in the range of values measured by Engstrom et al. (2009) for Lake Pepin sediments.

Table 26. Particle Enriched inorganic P concentration after their exposure to river water P concentration of 0.5 mg/L. Particle enrichment removes all sand (ER) as well as organic P and sand bound P.

Bank Material ID#	TP mg/kg after 0.5 exposure	Inorganic P with organic P and sand P removed	Particle ER	Particle Enriched Inorganic P on clay/silt (mg/kg)
100	411	319	1.64	523
106	475	337	1.92	647
130	529	449	1.60	718

Table 27. Particle Enriched inorganic P concentration after their exposure to P river water concentration of 1.0 mg/L. Particle enrichment removes all sand (ER) as well as organic P and sand bound P.

Bank Material ID#	TP mg/kg after 1.0 exposure	Inorganic P with organic P and sand P removed	Particle ER	Particle Enriched Inorganic P on clay/silt (mg/kg)
100	425	332	1.64	548
106	484	346	1.92	667
130	589	510	1.60	816

Table 28. Particle Enriched inorganic P concentration after their exposure to P river water concentration of 2.0 mg/L. Particle enrichment removes all sand (ER) as well as organic P and sand bound P.

Bank Material ID#	TP mg/kg after 2.0 exposure	Inorganic P with organic P and sand P removed	Particle ER	Particle Enriched Inorganic P on clay/silt (mg/kg)
100	449	357	1.64	586
106	500	363	1.92	693
130	703	623	1.60	997

Table 29. Particle Enriched inorganic P concentration after their exposure to P river water concentration of 3.0 mg/L. Particle enrichment removes all sand (ER) as well as organic P and sand bound P.

Bank Material ID#	TP mg/kg after 3.0 exposure	Inorganic P with organic P and sand P removed	Particle ER	Particle Enriched Inorganic P on clay/silt (mg/kg)
100	469	376	1.64	616
106	513	376	1.92	718
130	809	729	1.60	1166

The above analysis shows that particle enrichment along with P adsorption by fine particles of bank materials from river water partially explains the increases in inorganic P concentration in Lake Pepin sediments post settlement period. In the above calculations, we had assumed only sand particles are remaining upstream of Lake Pepin, which is reminiscent of sand bar development. However, in his report, Engstrom and Almendinger (2000) also showed that mean particle size in the Lake Pepin cores decreased slightly from 1850 to 1970; meaning a greater percent was made up of finer grained material (more clay and a little less in silt). We used this information and ran another sensitively analysis to factor in additional particle enrichment. In this sensitivity analysis, we assumed that in addition to the sand fraction 10%, 20% and 30% of the silt was also remaining behind in the river system possibly due to lock and dams. This means a further increase in the

enrichment ratio of bank material (ER_1 , ER_2 and ER_3) and thus in the inorganic P concentration of the lake sediment derived from bank materials. When we incorporate the new enrichment ratios with historical dissolved P river concentrations at 0.5 mg/L and 1.0 mg/L, the fine particle inorganic P range becomes 625-855 mg/kg and 653-969 mg/kg, respectively (Tables 30 and 31). This range of enriched inorganic P explains more than half of the maximum inorganic P concentrations reported for Lake Pepin sediments for the post settlement period (Engstrom et al., 2009). Although these calculations do not fully explain the peak inorganic P concentration (1300 mg/kg averaged over 2 replications and five transects) measured in Lake Pepin sediments in 1970, they go a long way towards explaining lake sediment inorganic P concentrations up to the 1950s.

Another factor that may explain the higher P concentrations in Lake Pepin sediment post 1850 is the presence of iron in STP effluents. As discussed earlier, iron and aluminum has a high affinity for binding with P. Prior to 1930, there was no treatment of waste water in Minnesota (Crohurst, 1932) and thus iron concentrations discharged to the river would have been similar to the iron concentration in the influent. Also, prior to separation of storm water in the Twin Cities, raw sewage was often discharge in rivers during high rainfall events which meant greater input of iron in river waters. Waste water analysis from Pigs eye plant in 1966 (Table 32) shows iron concentration in the influent varied from 1.8 to 6.1 mg/L with an average of 3.1 mg/L. Iron removal efficiency was reported at 5.5% with iron concentration in the effluent varying from 1.0 to 1.7 mg/L and an average concentration of 1.4 mg/L (FWPCA, 1966). Although there was no reporting of aluminum concentration in the waste water, there must have been some level of aluminum in the effluent from the STP. The presence of both iron and aluminum may have contributed to increased P adsorption by sediments in the river. A dramatic decrease in NaOH extract P after 1970 (Engstrom et al., 2009) further attests to reduced P and other (iron and aluminum) pollution in river waters which in turn helped reduce P adsorption by river sediments (see Fig. 8).

In summary, the above analysis shows that particle enrichment of bank material is sufficient to explain the inorganic P concentrations found in Lake Pepin sediment pre-

settlement period. In the post-settlement period, enhanced particle enrichment (settling of sand plus some silt) along with P adsorption from river waters (domestic and industrial P pollution) by finer particles of bank materials are the likely mechanisms for higher inorganic P concentration in Lake Pepin sediments. Presence of iron and possibly aluminum in the waste water effluent in post settlement period are additional factors that may have contributed to further increase in P adsorption by fine particles of bank materials and in turn explain P increase in Lake Pepin sediments. This aspect needs further research.

Table 30. Inorganic P concentrations of three till bank materials after particle enrichment with removal of sand as well as 10% (ER1), 20% (ER2), and 30% (ER3) silt and adsorption at river water P concentration at 0.5 mg/L.

Bank Material ID#	TP at 0.5 mg/L (mg/kg)	Inorganic P with organic P and sand P removed	Particle ER ₁	Particle Enriched Inorganic P #1 (mg/kg)	Particle ER ₂	Particle Enriched Inorganic P #2 (mg/kg)	Particle ER ₃	Particle Enriched Inorganic P #3 (mg/kg)
100	411	319	1.74	555	1.84	587	1.96	625
106	475	338	2.03	686	2.16	730	2.31	781
130	529	450	1.69	761	1.80	810	1.90	855

Table 31. Inorganic P concentrations of three till bank materials after particle enrichment with removal of sand as well as 10% (ER1), 20% (ER2), and 30% (ER3) silt and adsorption at river water P concentration at 1.0 mg/L.

Bank Material ID#	TP at 1.0 mg/L (mg/kg)	Inorganic P with organic P and sand P removed	Particle ER ₁	Particle Enriched Inorganic P #1 (mg/kg)	Particle ER ₂	Particle Enriched Inorganic P #2 (mg/kg)	Particle ER ₃	Particle Enriched Inorganic P #3
100	425	333	1.74	580	1.84	613	1.96	653
106	484	347	2.03	704	2.16	750	2.31	802
130	589	510	1.69	862	1.80	918	1.90	969

Table 32. Iron and total phosphate concentrations (mg/L) from the Minneapolis-St. Paul (Pigs Eye) sewage treatment plant (STP) (after FWPCA, 1966).

Constituent	Influent Concentration (mg/L)			Effluent Concentration (mg/L)			Average Removal Efficiency (%)
	Maximum	Average	Minimum	Maximum	Average	Minimum	
Iron	6.1	3.1	1.8	1.7	1.4	1.0	5.5
Total Phosphate	21.2	13.8	4.8	22.4	13.5	3.6	-

Conclusions

Phosphorus is an essential element for plant growth but is also a persistent pollutant in the aquatic systems. Since it is found in limited quantities within the United States, efforts have been made in the agricultural community on prudent applications of phosphate fertilizers using soil P test values as well as in finding ways to minimize its losses from farmlands.

Both the Minnesota River and Lake Pepin have a long history of water quality impairments in terms of sediment and phosphorus. Investigations into these questions have concluded that slumping river banks within the GBERB are a major source of sediments in these water bodies. Since P is a limiting nutrient in both these freshwater systems, the above finding has led us to a question: what role bank materials may be playing in river water chemistry especially in terms of phosphorus transport? Specific goals of this research were: (1) Whether river bank materials are inherently a significant source of P in the Minnesota River and Lake Pepin, (2) What is the potential of river bank materials in Blue Earth County to adsorb P from river waters, and (3) To what extent particle enrichment along with P adsorption explains inorganic P/TP concentrations in Lake Pepin sediments for both pre-and post-settlement periods.

Based on the analysis completed in this thesis, we make the following conclusions. The bank materials are inherently high in TP content (400 mg/kg) but they are low in Bray and Olsen test P values which mean that the P is tied up in forms not readily available to plants and microbes. The bank materials also have very low organic matter levels relative to the surface prairie and agricultural soils, the predominant land uses in the study area in pre-and post-settlement periods, respectively. Total P content of random bank materials was similar to TP content of samples from deep soil cores taken by Minnesota Geological Survey thus indicating that random bank samples were representative of the materials in tall sloughing banks in the study area.

Steep slope of the adsorption isotherms as well as the high S_{\max} values (520±95 mg P/kg bank material) of the Langmuir adsorption isotherm suggested that bank materials have a high affinity as well as high capacity to adsorb P. Additionally, adsorption-desorption-

adsorption (ADA) and desorption-adsorption-desorption (DAD) experiments demonstrated strong P binding ability of the bank materials but a limited P desorption potential.

EPC₀ of bank materials was very low thus suggesting that under current conditions river bank materials will continue to scavenge P from the river waters and then act as a carrier and later as a source of P in Lake Pepin. To remedy this situation, we conclude that the dissolved P in river waters needs to be below 0.1 mg/L (linear fit) to 0.15 mg/L (Langmuir isotherm fit) to tip the scale from acting as a carrier to acting as a source. The EPC₀ values of the bank materials were lower than those found in downstream sediments thus suggesting some enrichment of the particles, mixing of sediments from surface agricultural soils and/or EPC₀ values changing when coming in contact with river waters. Additional research is needed to sort this out.

Sequential P extraction showed that GBERB river bank materials have a strong calcium-dominated TP signal. In comparison surface prairie soils were dominated with organic P while surface agricultural soils had even distribution of aluminum/iron-P, calcium and organic-P. Minnesota River sediment showed the similar uniform distribution of P as the agricultural soils but P distribution in Lake Pepin sediments was slightly different. Some of the differences between the source materials (banks, prairie and agricultural soils) and sediments (Minnesota River and Lake Pepin) may be due to particle enrichment, P adsorption during sediment transport, as well as mixing of sediment from various sources. We conclude that further work is needed to explore how various P fractions in source materials change as they tumble down stream to Lake Pepin.

We also explored the role of river bank materials in explaining inorganic P concentrations of Lake Pepin sediments in both pre- and post-European settlement periods. This was done by using the concepts of particle enrichment (sand remaining behind) as well as P adsorption by bank materials in conjunction with historic P pollution of river waters upstream of Lake Pepin. Particle enrichment of river bank sediments explained inorganic P level (500-700 mg/kg) in Lake Pepin prior to 1850. Adsorption from historic river P pollution (0.5 and 1.0 mg P/L) along with settling of sand and some silt explained to a

large extent the increasing levels of inorganic P in lake sediments (625-969 mg/kg) since 1850. However, these factors were unable to explain the higher inorganic P level in Lake Pepin sediments (average of 1300 mg/kg over five transects) in 1970s. This may be partially due to lack of accurate historic P concentrations in rivers during the peak period of P use in detergents and/or some contributions from agricultural lands. We conclude that sediment enrichment and P adsorptions from river are the major drivers of increasing inorganic P levels in Lake Pepin sediments since 1850.

Overall, river bank materials are a significant source of total P but not that of dissolved P to both the Minnesota River as well as to Lake Pepin. As these materials tumble downstream, they likely encountered anthropogenic P pollution in rivers which in turn raised their adsorbed P concentrations. This adsorbed P is likely a continuous source in Lake Pepin.

In recent years there have been major improvements in the point source pollution, specifically the input of P in rivers. The adoption of conservation and best management practices has also increased within the MRB and GBERB. Data documenting the positive impacts of these efforts on improved water chemistry to the Minnesota River and then Lake Pepin has yet to be conclusively conducted. However, based upon the bank material adsorption isotherms one way to prevent sequestering of dissolved P from river waters is to make sure dissolved P concentrations in river water are less than EPC_0 values of bank materials.

Future Research

Although this thesis research resolved some questions, it also raised a series of questions that needs further exploring. Those questions are as follows:

1. Although EPC_0 values of bank materials is very low relative to that of surface agricultural soils, previous research by James et al. (2002), James and Barko (2004), and James and Larson (2008) has shown that EPC_0 of the river sediments increases from a low value of 0.074 mg/L in Redwood River to 0.117 mg/L in the Lower Minnesota River and 0.155 mg/L in Lake Pepin. The question: What are the reasons for change in EPC_0 values of sediments in the Minnesota River as measured by James in his studies? Is this increase in EPC_0 downstream a reflection of the sources of sediments, particle enrichment, or increase in P concentration of the river water along the way? In other words, does EPC_0 value of river sediments change with river water P concentrations, more localized P inputs, or changing sediment sources? If so, how fast?
2. This research showed that distribution of various P fractions in surface agricultural soil and the Minnesota River sediment was different than those of the bank material or the Lake Pepin sediments. In agricultural soils and the Minnesota River sediments, there was no predominant P fraction i.e. calcium bound P, iron/aluminum bound P, organic P were nearly equally distributed. The question is: What are the reasons for change in P fraction distributions as the bank materials tumble downstream in the Minnesota River towards Lake Pepin?
3. The P content of sand particles remaining in sand bars was high (~180 mg P/kg of sand). Although its soil test P values were low both with Bray and Olsen P tests, they were similar to the soil test P values of sandy soils. Since there was a significant flow of algae from the Minnesota River to downstream locations during 2012 (a low flow year), a question has been raised: What is the nature of P in sand particles and can that be partially responsible for growth of these algae in the Minnesota River during low flow periods?

4. Generally, there is a lack of readily available information on historical P concentrations in river waters in Minnesota. Further research is needed to look into old historical records or estimate the historical P concentration in river waters in some other ways, such as correlation between dissolved P and BOD, in order to assess how river P concentration may have impacted inorganic P in lake sediments.

5. James (2010) found interesting trends in the river sediment in regards to particle sizes. For example, the sediment concentrations of TP, loosely bound, iron, aluminum, and organic P increased with decreasing particle diameter. In contrast, calcium bound P concentrations remained constant. Sequential P fraction by particle size for a variety of sediment sources such as bank materials, agricultural soils, soils along ravines and drainage ditches, sediments in various rivers will help further explain adsorption processes as well as help improve enrichment calculations.

6. Since iron has a strong affinity for phosphorus, additional research on the role of iron and possibly aluminum in river waters on P adsorption by sediments needs further quantification.

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Appendices

Appendix A.

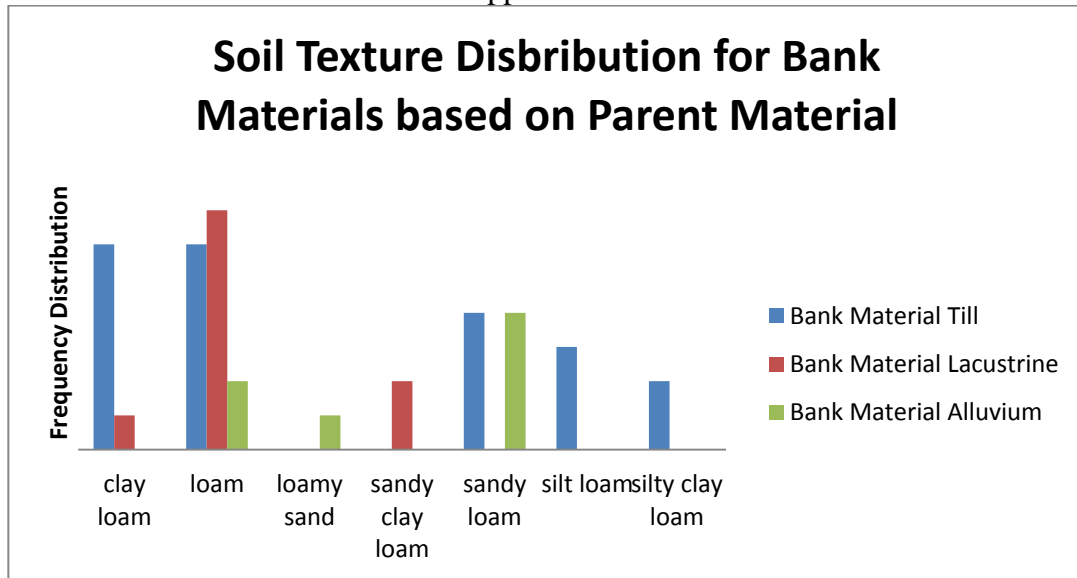


Figure A1. USDA textural class of bank materials based upon parent material

Appendix B. Adsorption/Desorption Studies and Adsorption Isotherms.

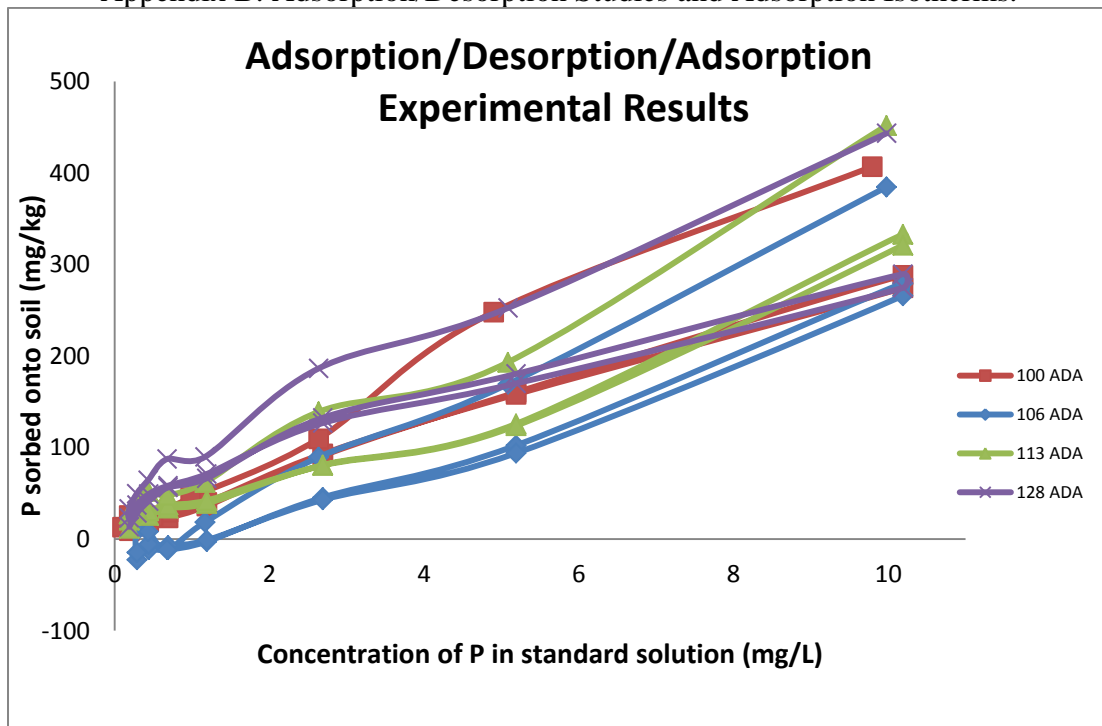


Figure B1. ADA, 3 Successive exposures: Adsorption run, followed by low P desorption and finally a second adsorption run.

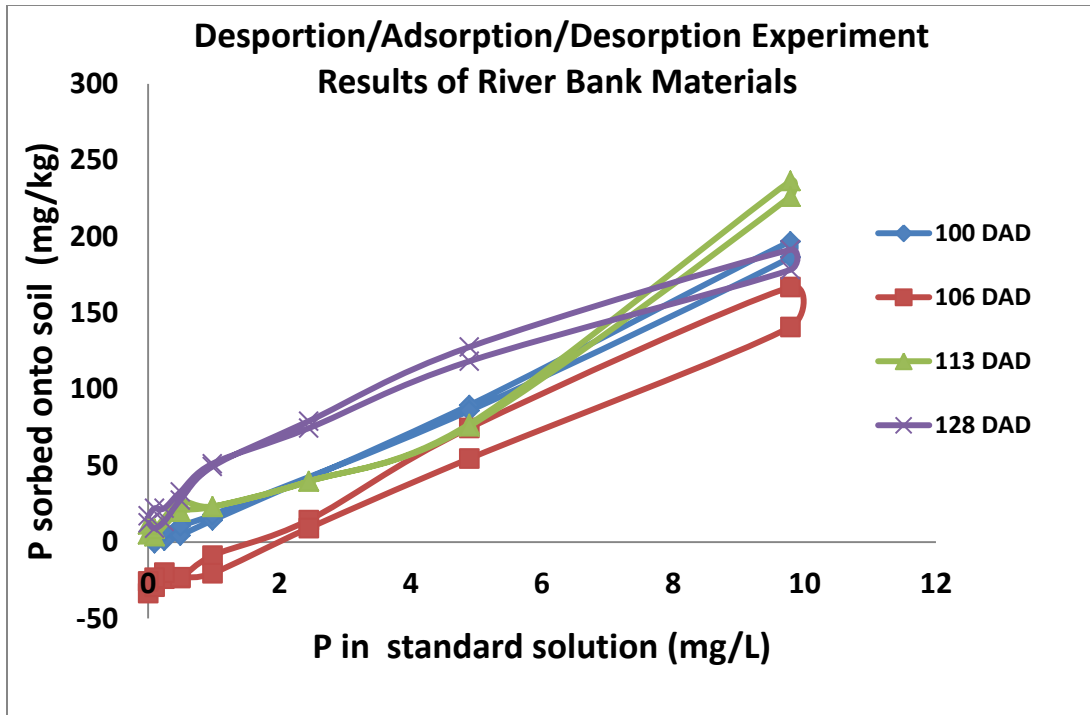


Figure B2. DAD, 3 Successive exposures: Low P water exposure followed by adsorption run, and finally a second desorption run.

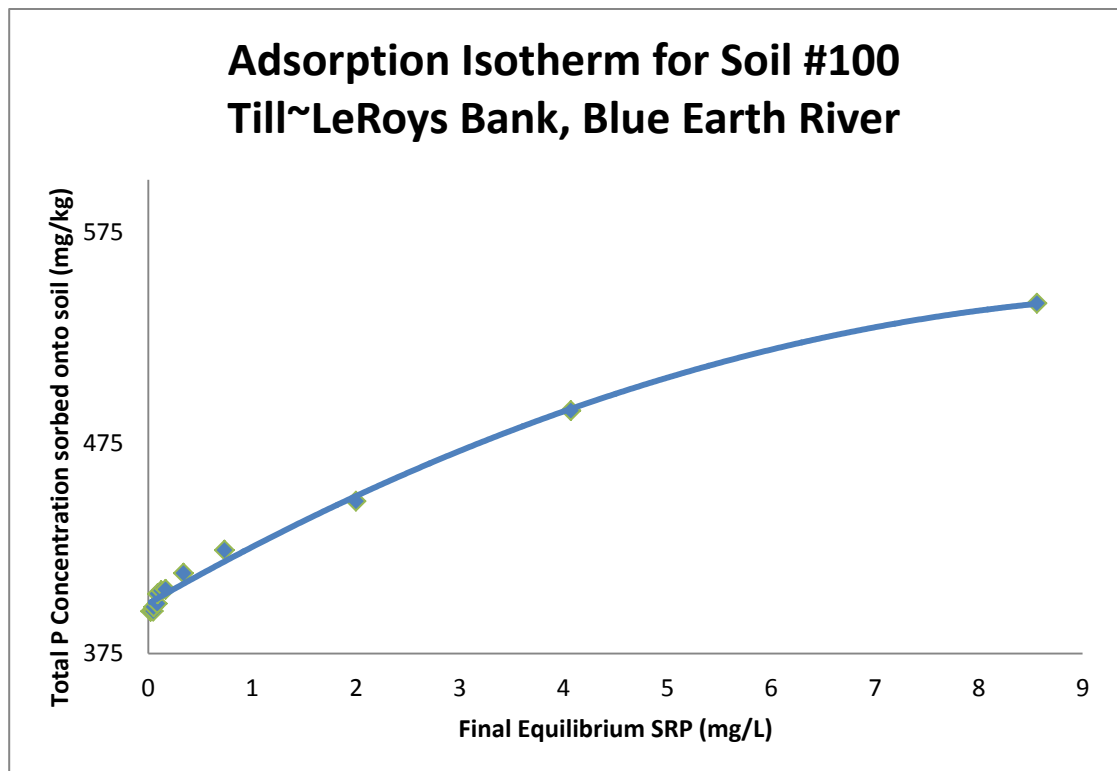


Figure B3. Adsorption Isotherm for Soil #100

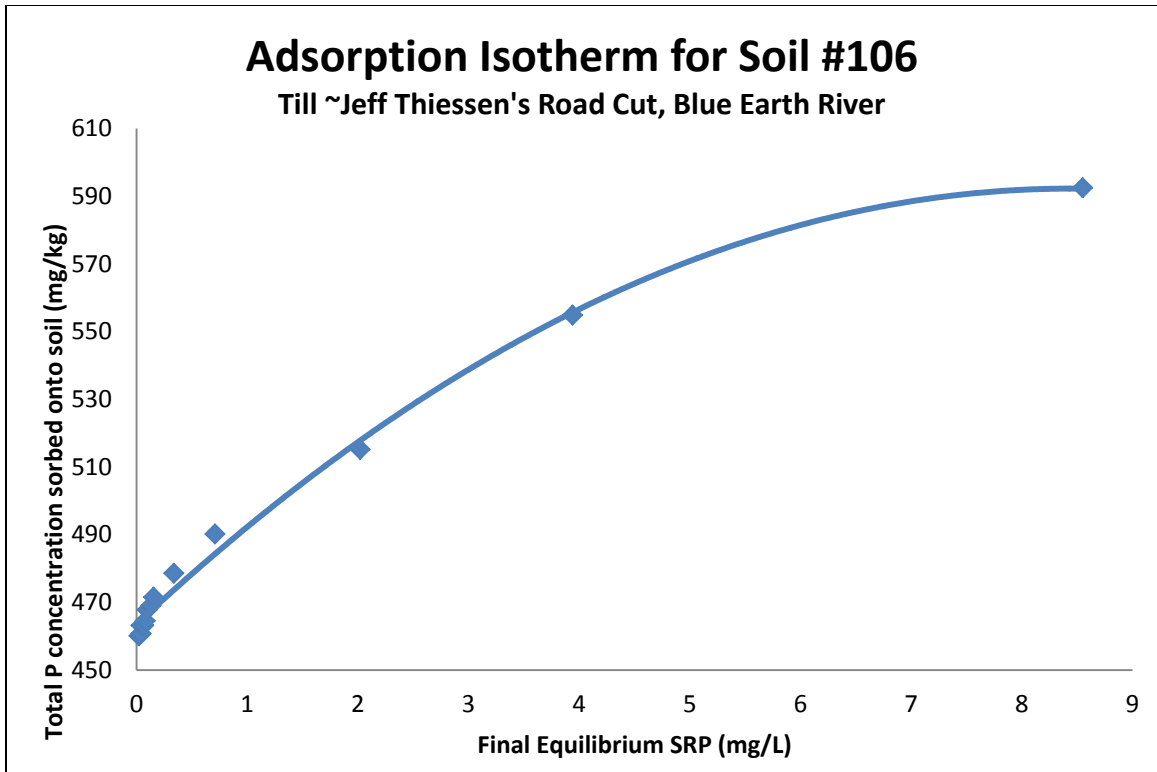


Figure B4. Adsorption Isotherm for Soil #106

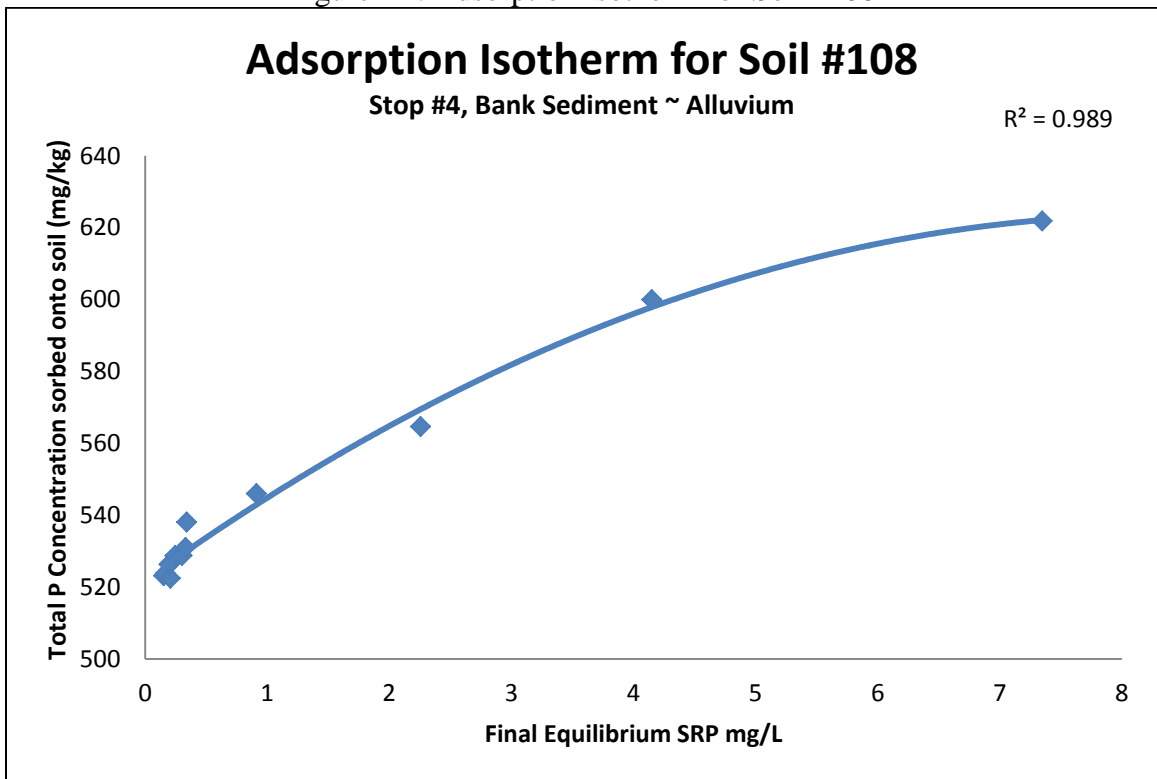


Figure B5. Adsorption Isotherm for Soil #108

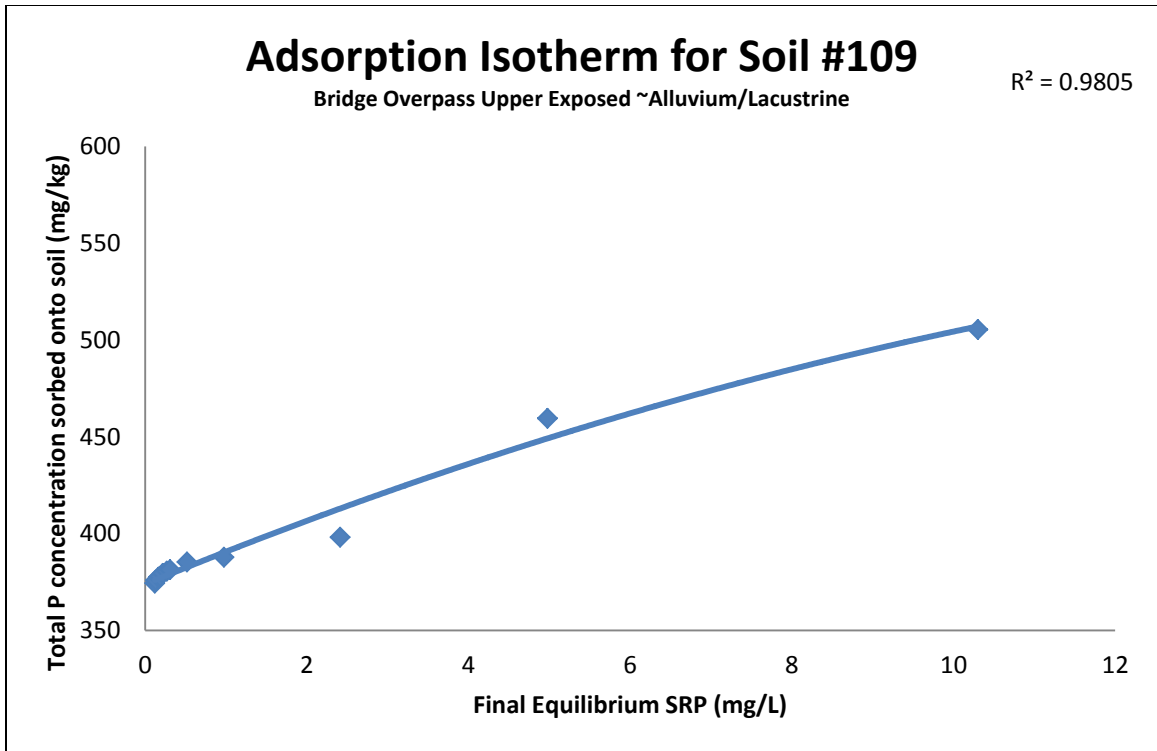


Figure B6. Adsorption Isotherm for Soil #109

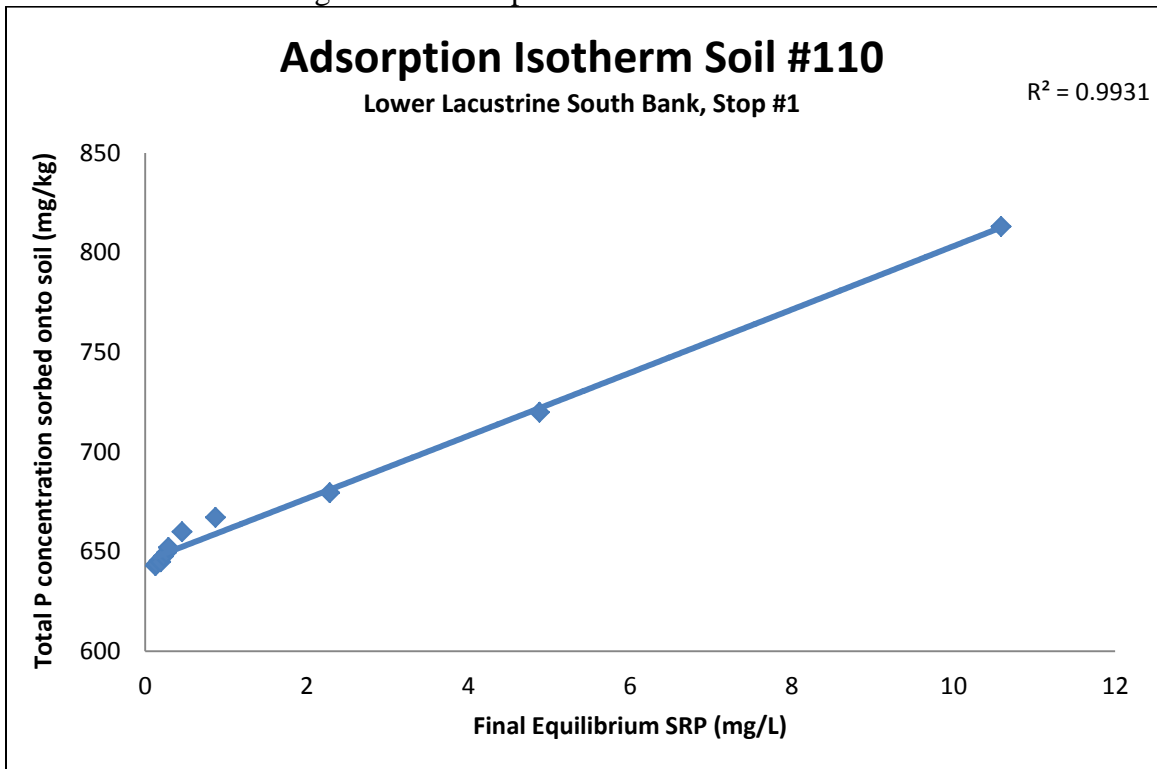


Figure B7. Adsorption Isotherm for Soil #110

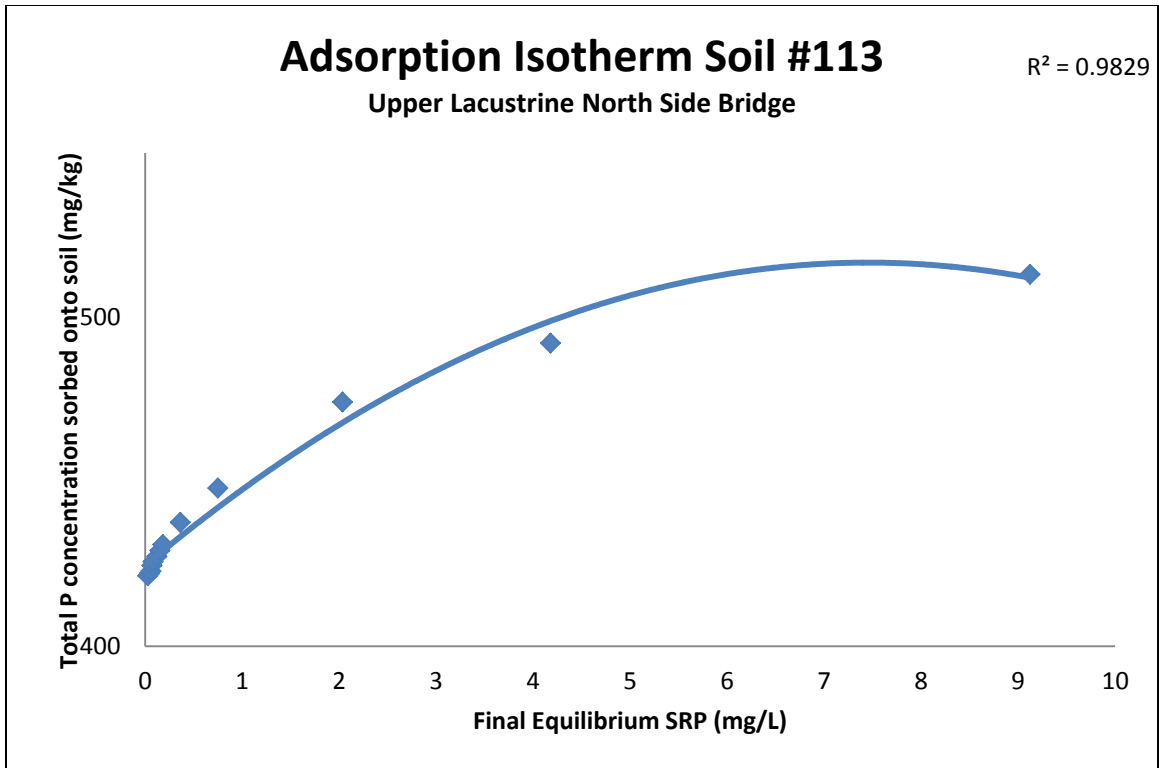


Figure B8. Adsorption Isotherm for Soil #113

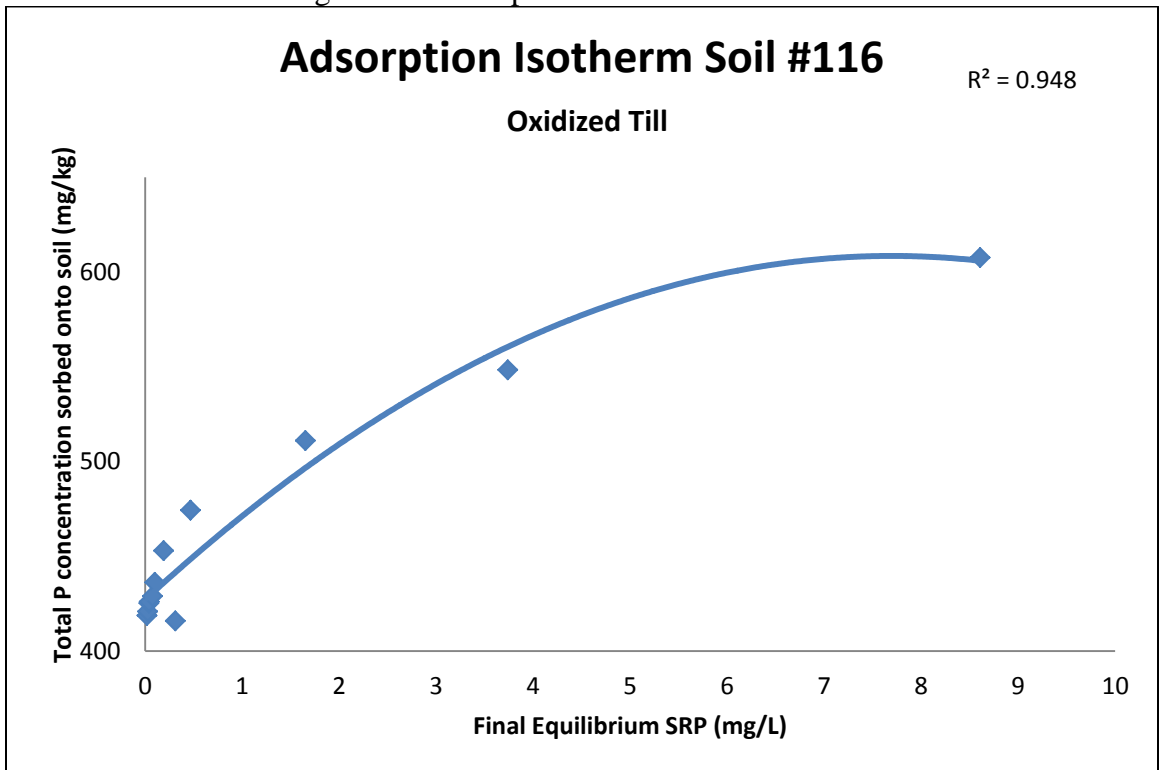


Figure B9. Adsorption Isotherm for Soil #116

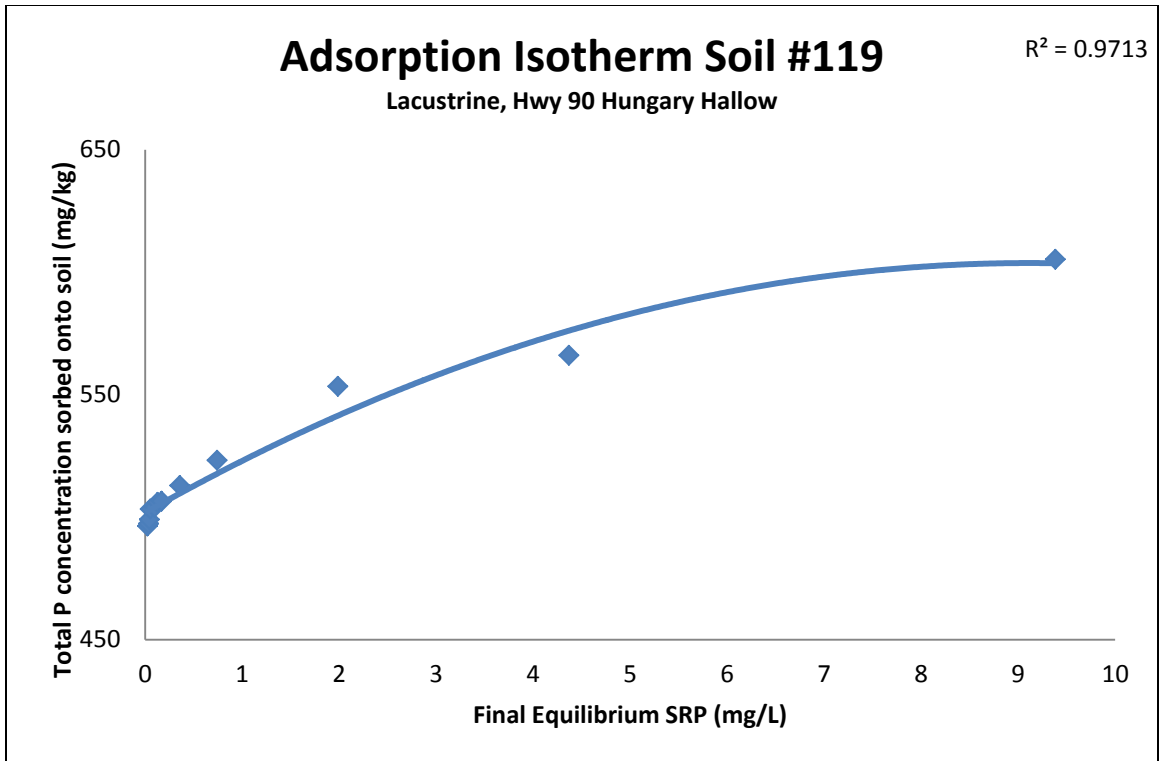


Figure B10. Adsorption Isotherm for Soil #119

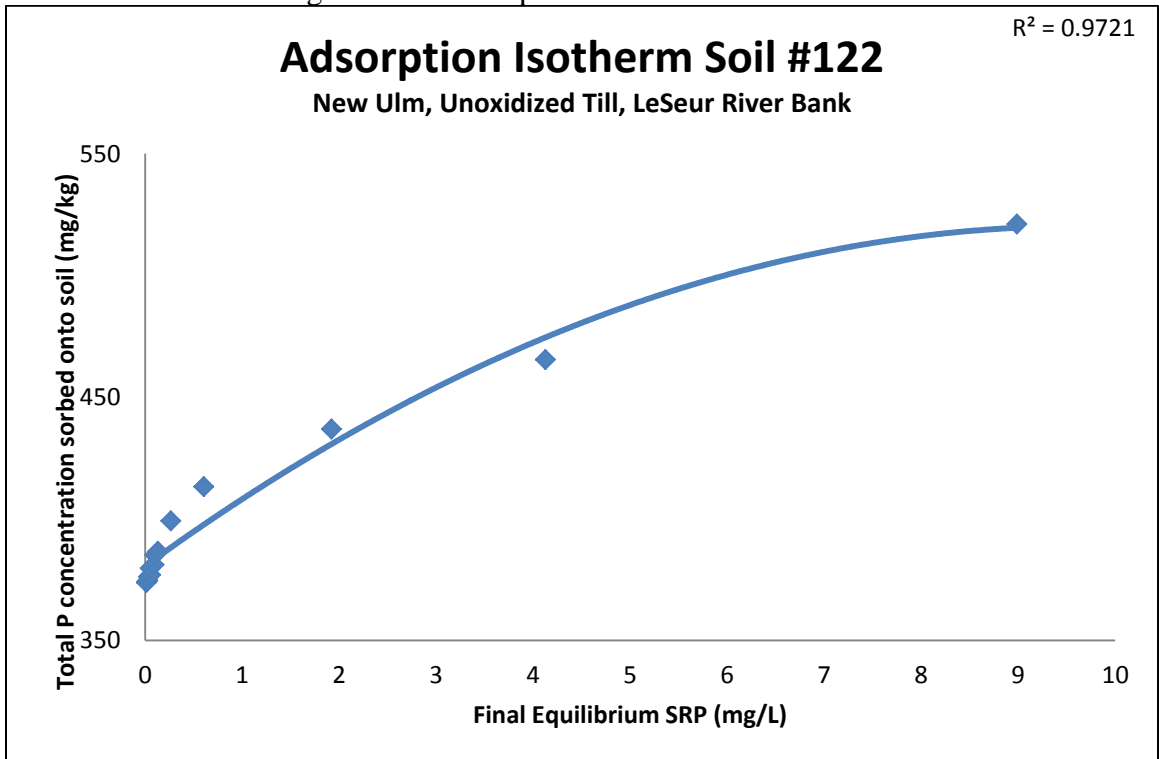


Figure B11. Adsorption Isotherm for Soil #122

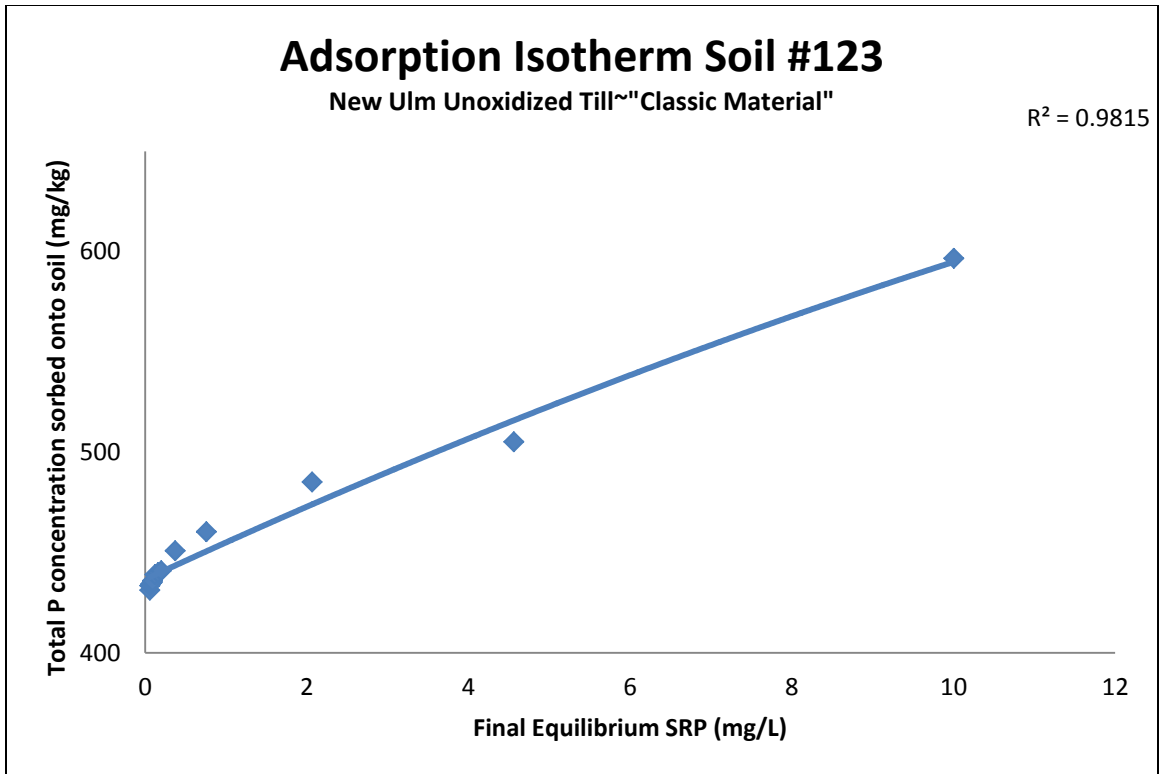


Figure B12. Adsorption Isotherm for Soil #123

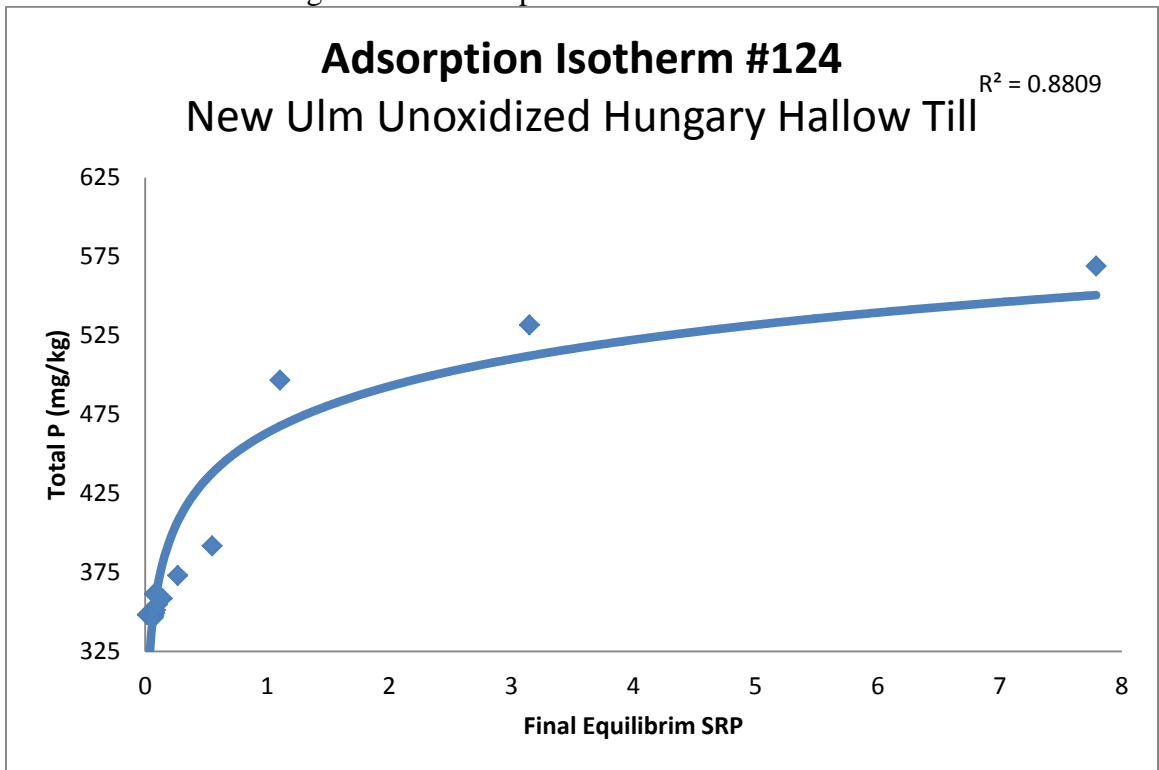


Figure B13. Adsorption Isotherm for Soil #124

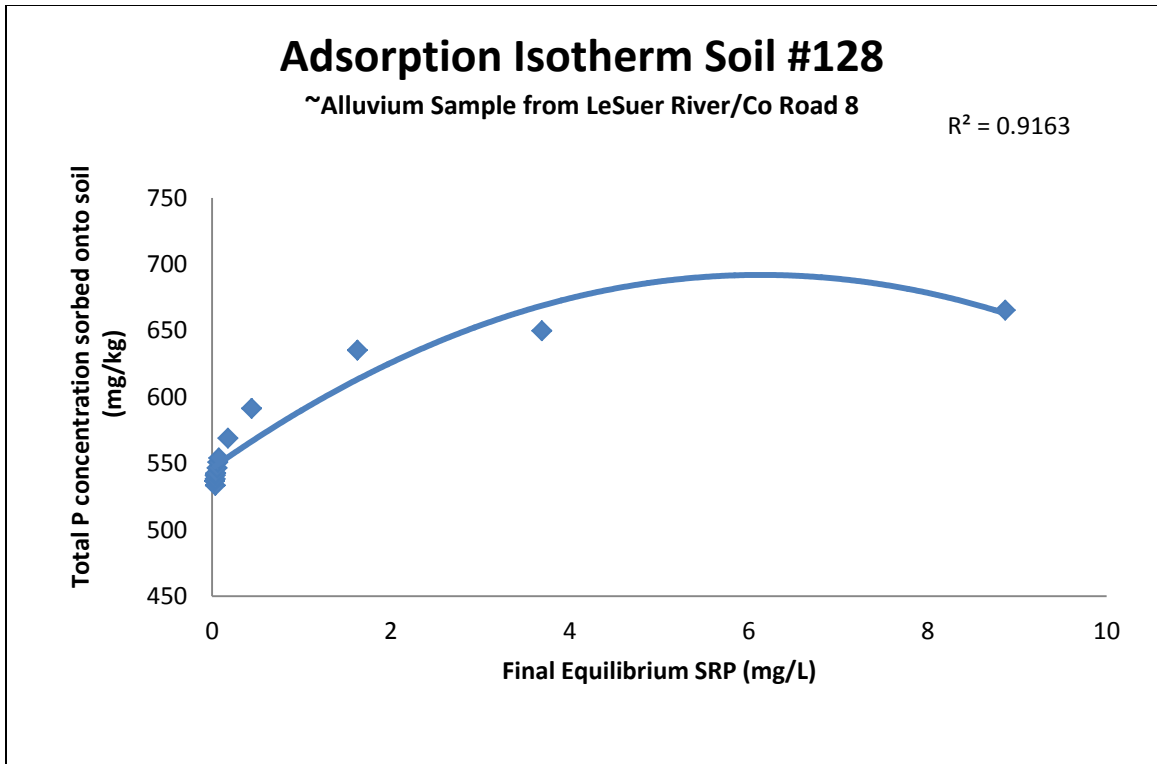


Figure B14. Adsorption Isotherm for Soil #128

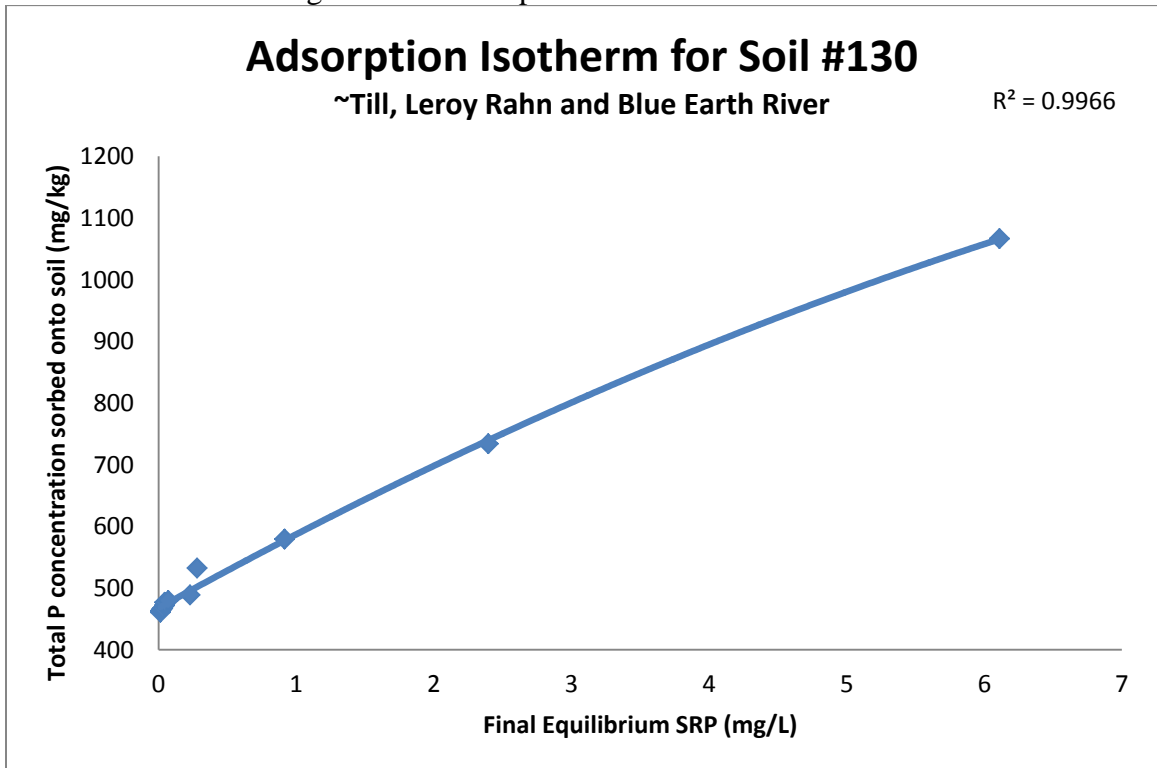


Figure B15. Adsorption Isotherm for Soil #130

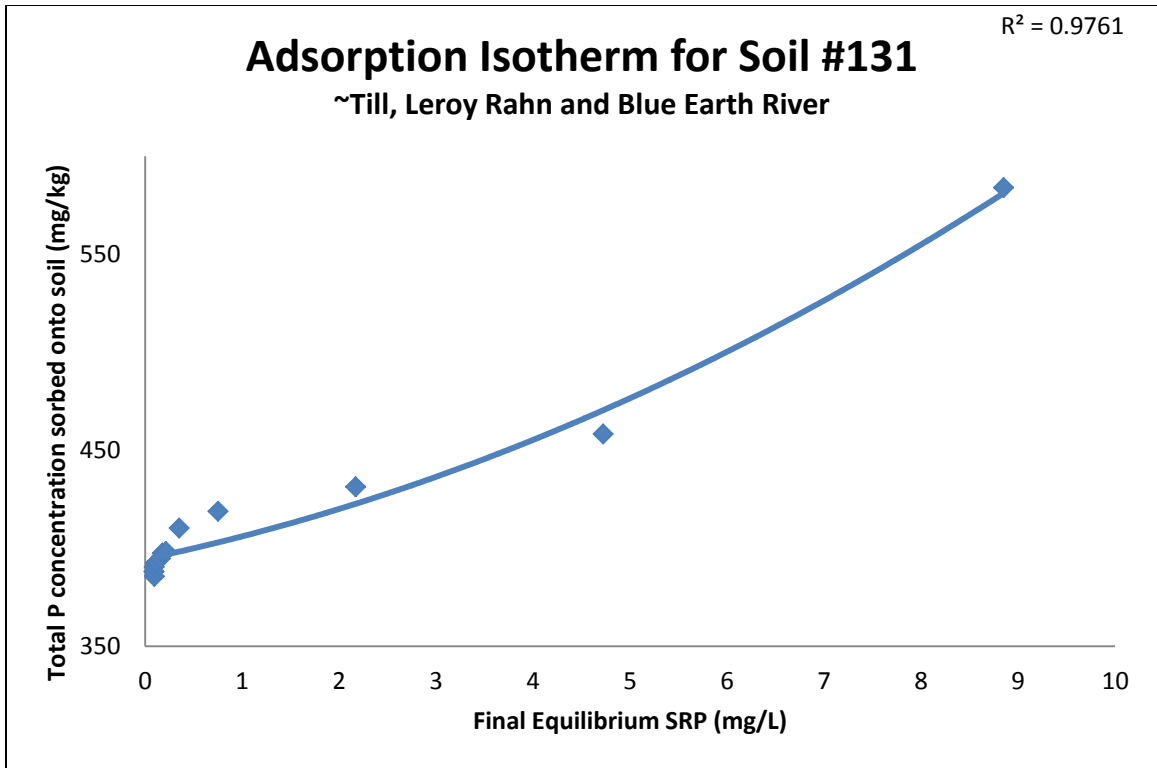


Figure B16. Adsorption Isotherm for Soil #131

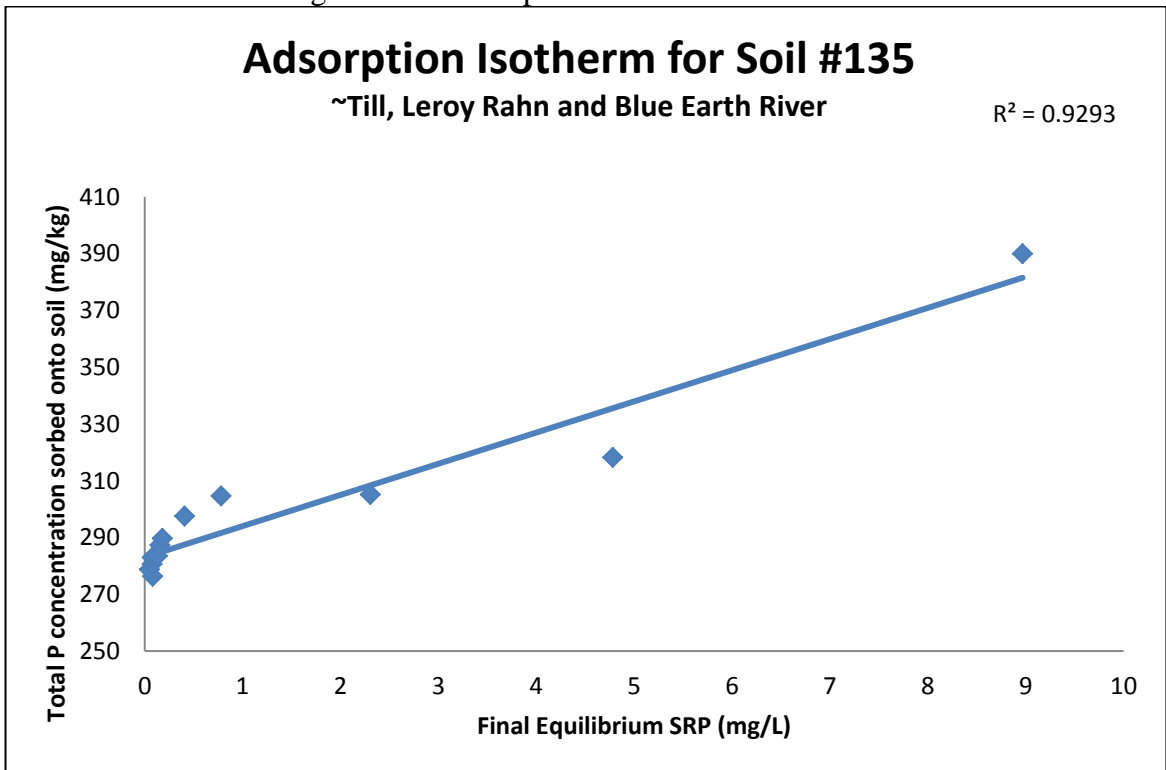


Figure B17. Adsorption Isotherm for Soil #135

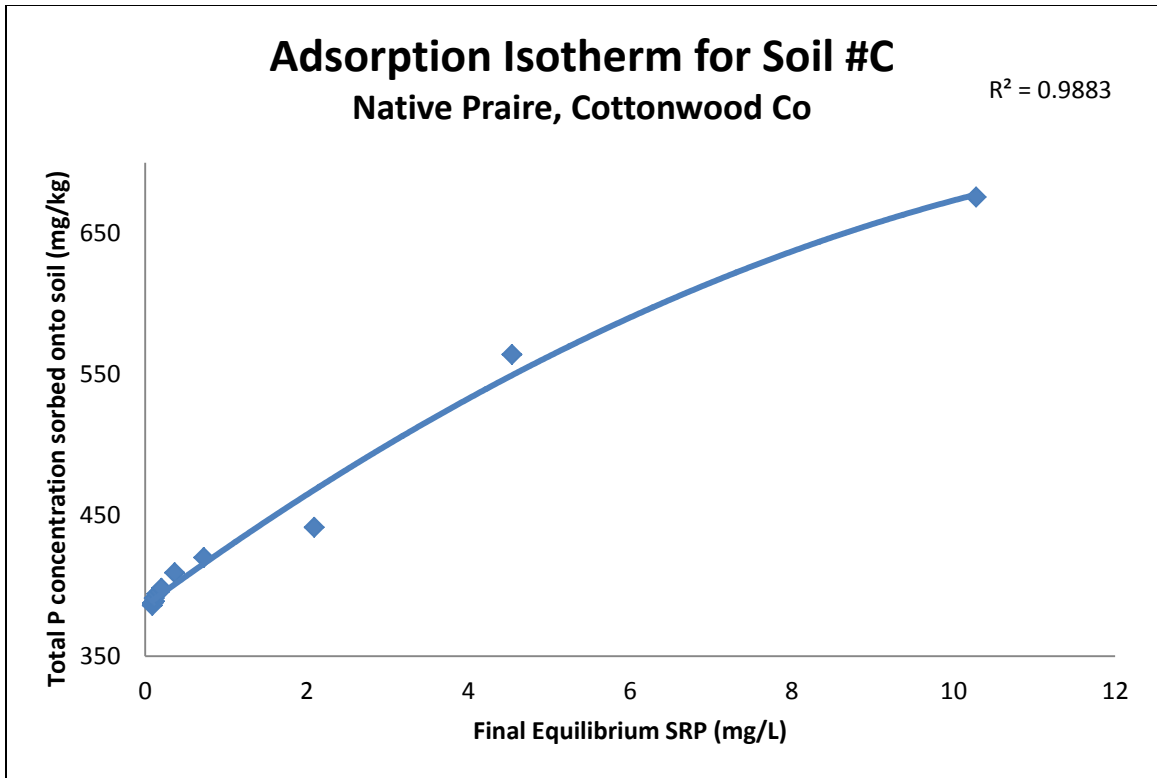


Figure B18. Adsorption Isotherm for Soil #C

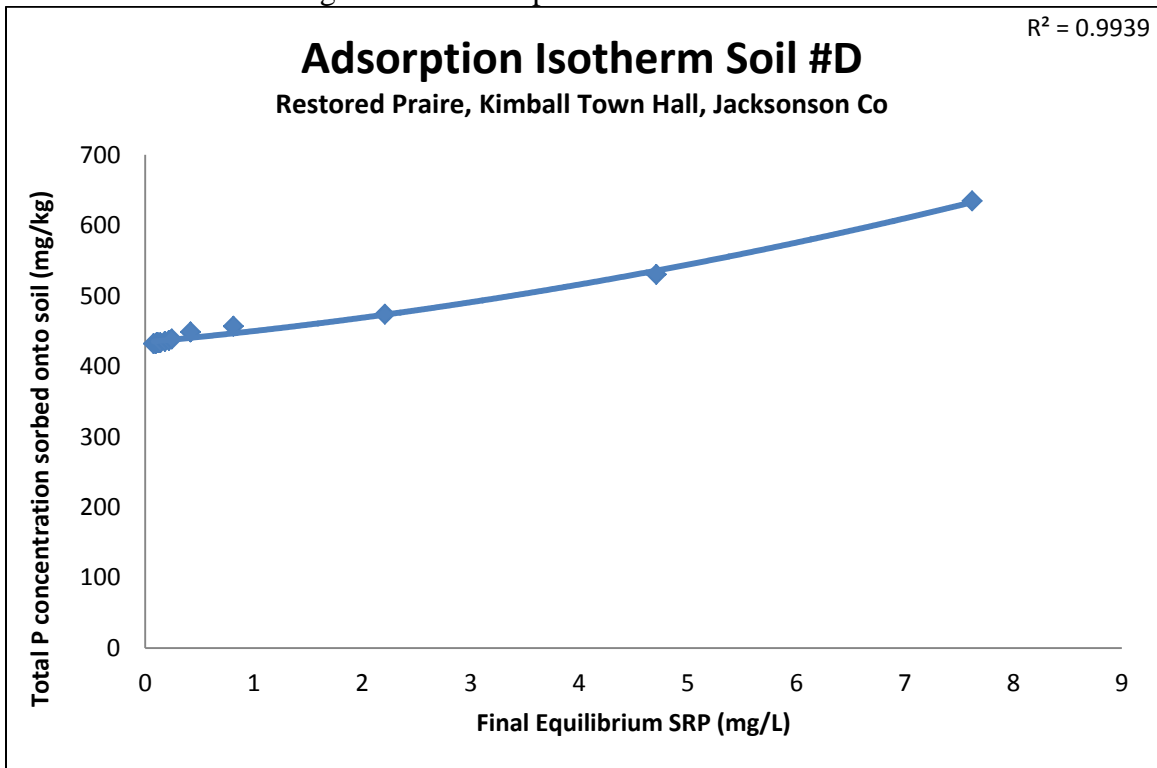


Figure B19. Adsorption Isotherm for Soil #D

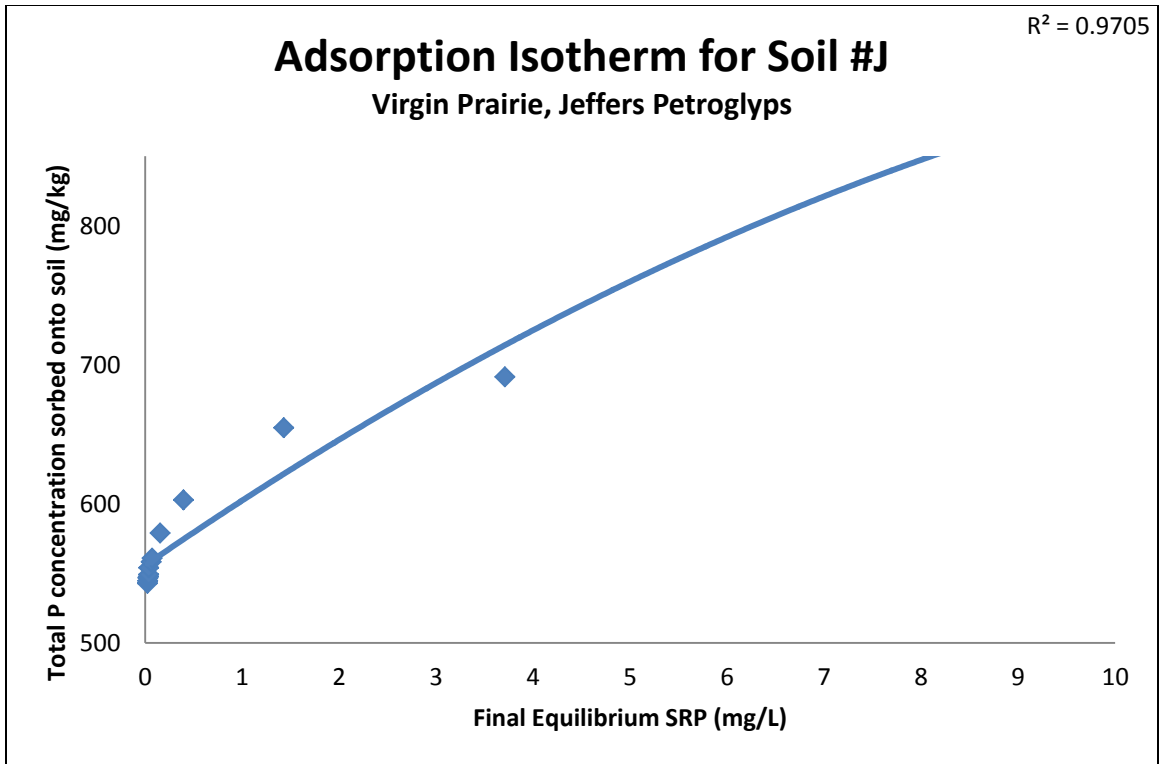


Figure B20. Adsorption Isotherm for Soil #J

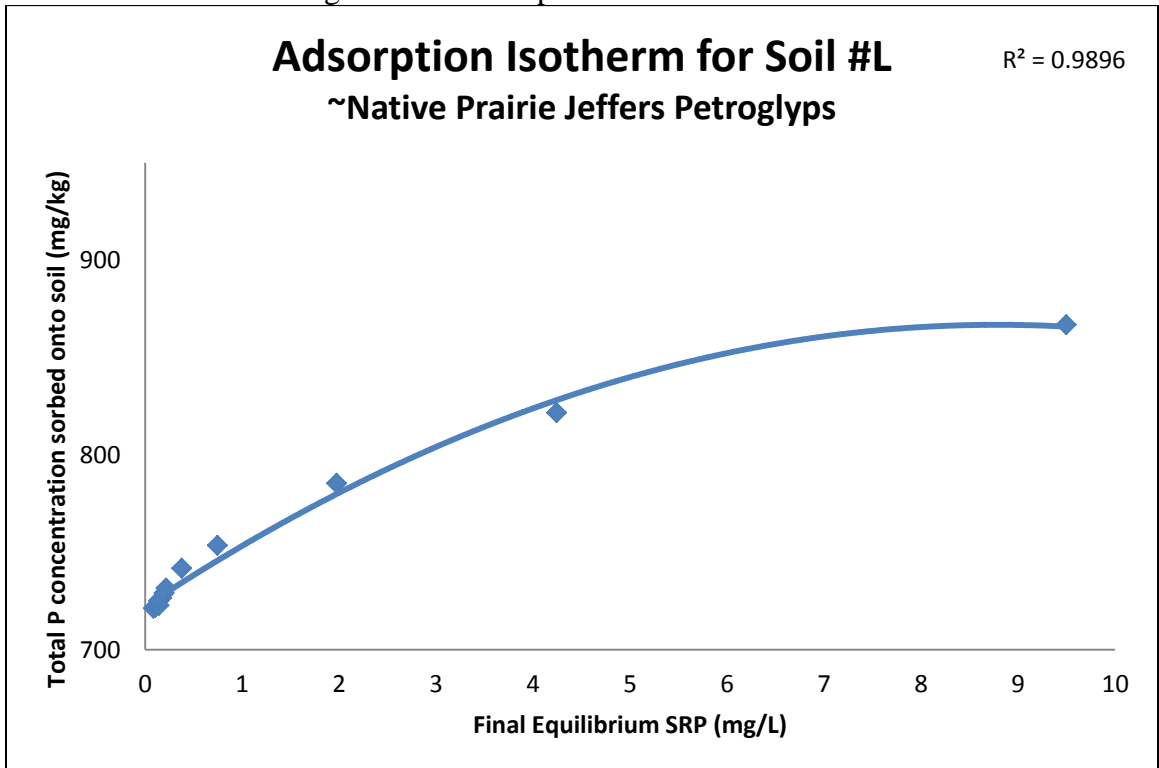


Figure B21. Adsorption Isotherm for Soil #L

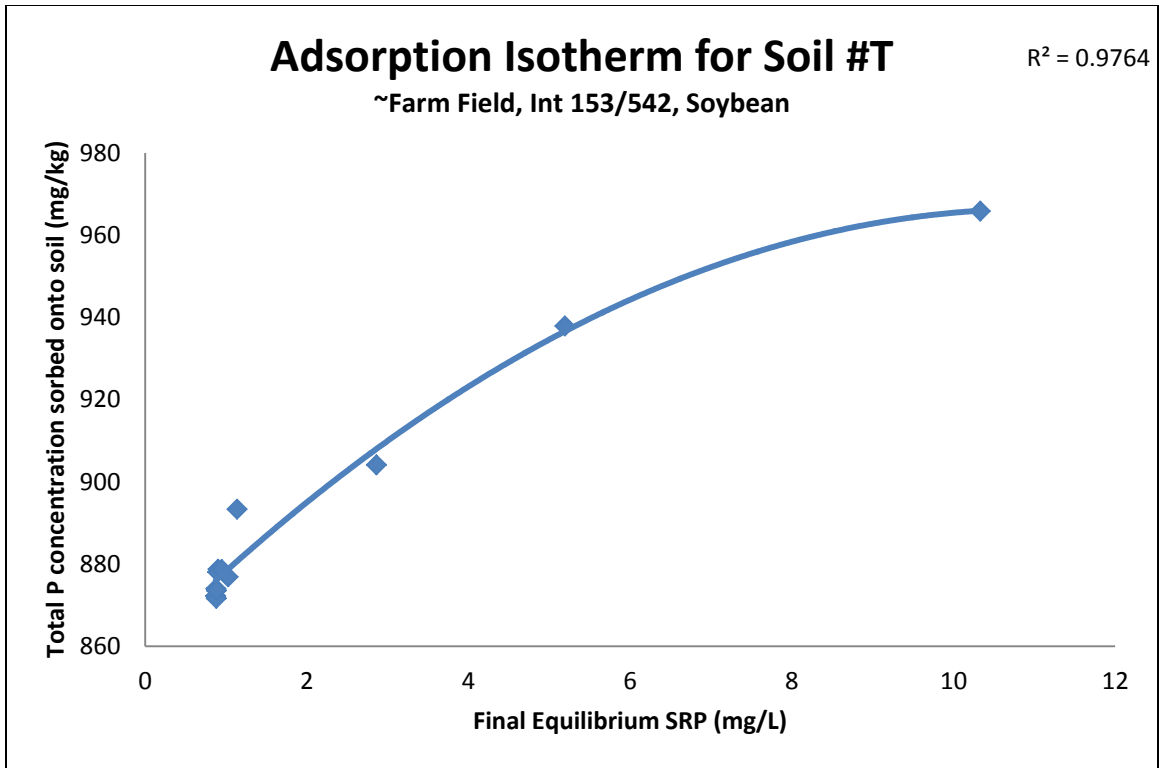


Figure B22. Adsorption Isotherm for Soil #T

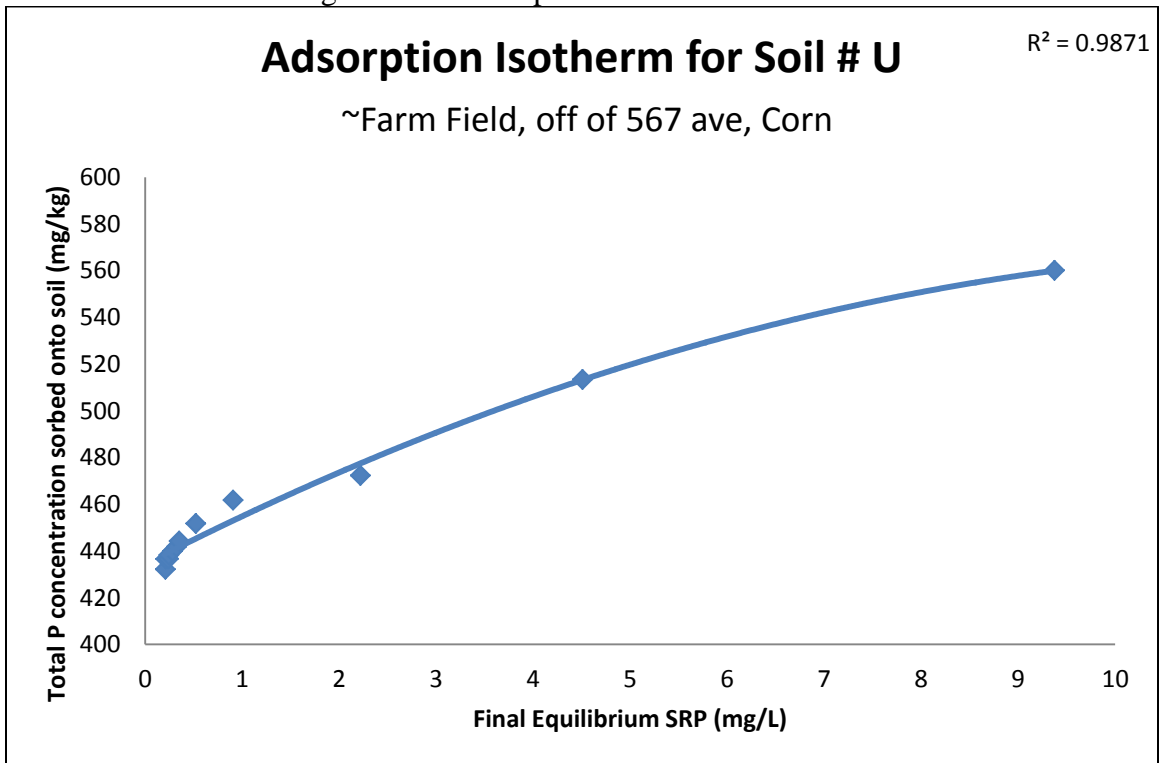


Figure B23. Adsorption Isotherm for Soil #U

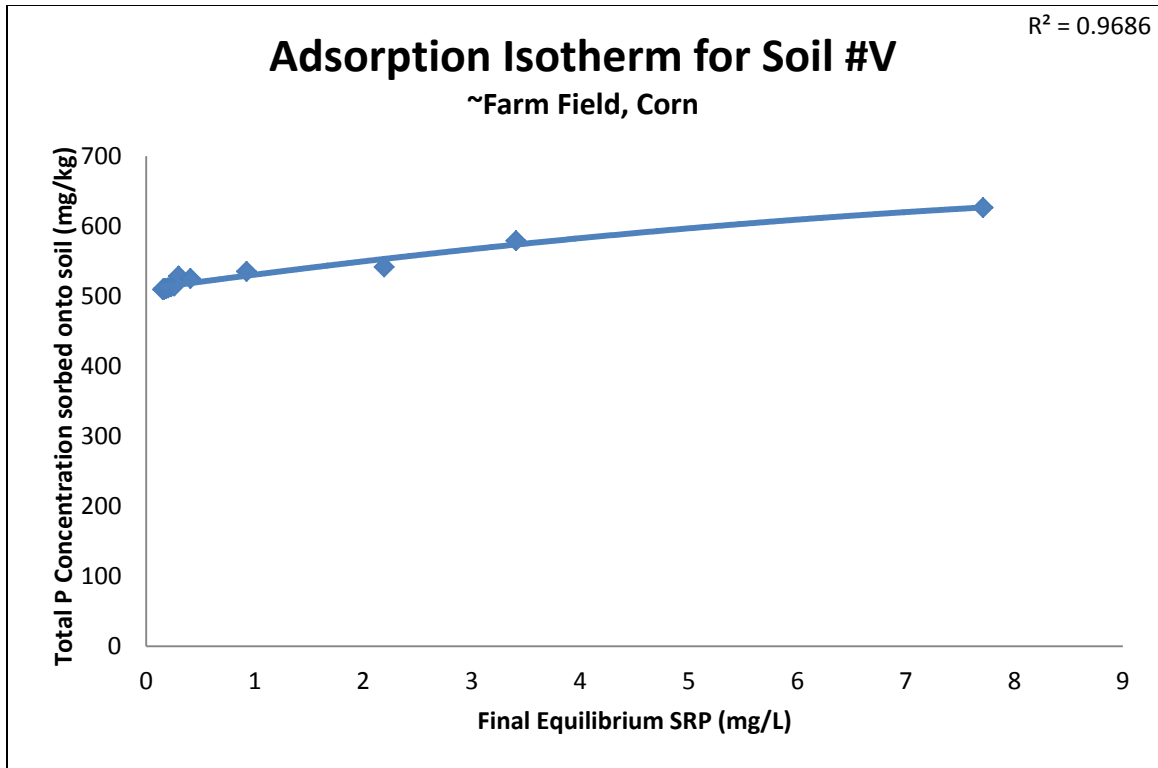


Figure B24. Adsorption Isotherm for Soil #V

Appendix C. Isotherm Individual Coefficients

Table C1. Freundlich Isotherm equation constants for bank materials and surface soils.

Soil ID	Parent material	K_f , Sorption coefficient (mg/kg)	Equilibrium coefficient (n)
100	Bank/Till	443	20
106	Bank/Till	505	30
108	Bank/alluvium	557	21
109	Bank/alluvium/lacustrine	393	11
110	Bank/lacustrine	673	16
113	Bank/lacustrine	463	26
116	Bank/Till	502	14
119	Bank/lacustrine	539	29
122	Bank/Till	406	18
123	Bank/Till	480	16

124	Bank/Till	456	9
128	Bank/alluvium	614	25
130	Bank/Till	682	8
131	Bank/Till	440	13
135	Bank/Till	308	25
C	Prairie	466	9
D	Prairie	478	11
J	Prairie	674	15
L	Prairie	774	24
T†	Agricultural	-	-
U	Agricultural	455	12
V	Agricultural	527	13

† Due to soils inherent soil properties there was limited adsorption in the range of solution concentrations tested in this study.

Table C2. Langmuir Isotherm equation constants for bank materials and surface soils.

Soil ID	Parent material	K_L	S_{max} (mg/kg)
100	Bank/Till	55	454
106	Bank/Till	110	454
108	Bank/alluvium	24	588
109	Bank/alluvium/lacustrine	4	476
110	Bank/lacustrine	35	714
113	Bank/lacustrine	105	476
116	Bank/Till	48	526
119	Bank/lacustrine	180	555
122	Bank/Till	73	454
123	Bank/Till	32	526
124	Bank/Till	30	476
128	Bank/alluvium	160	625

130	Bank/Till	50	66
131	Bank/Till	23	476
135	Bank/Till	44	322
C	Prairie	19	526
D	Prairie	9	555
J	Prairie	150	666
L	Prairie	40	833
T†	Agricultural	-	-
U	Agricultural	6	526
V	Agricultural	8	625

† Due to soils inherent soil properties there was limited adsorption in the range of solution concentrations tested in this study.

Appendix D. Deep soil core SC-8

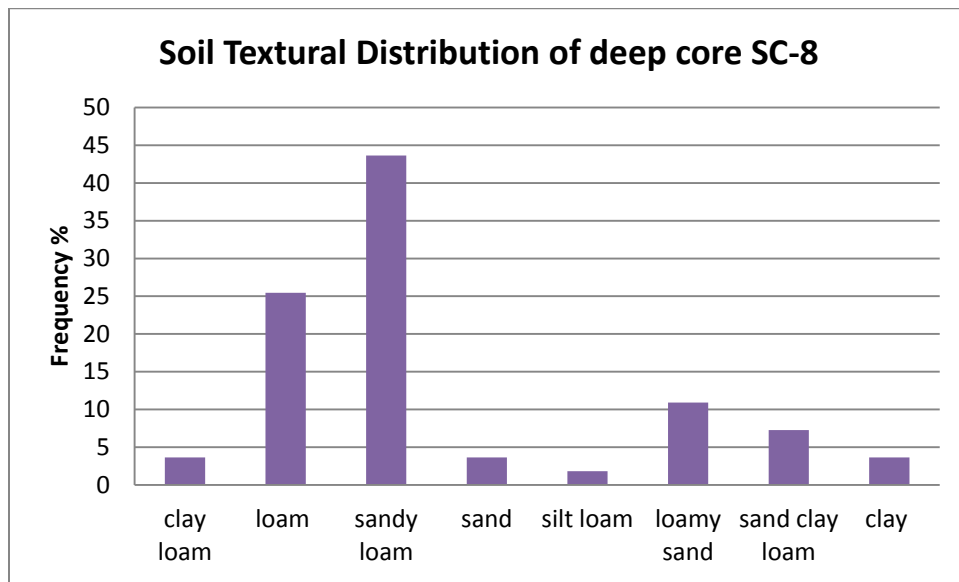


Figure D1. Frequency distribution of soil texture from deep soil core SC-8. Predominate texture is sandy loam and loam.

Table D1. Bulk density and total P average and standard deviation for Blue Earth county deep soil core SC-8. Broken up by soil texture type.

Material Texture	Bulk Density	total P
	Average \pm Standard Deviation	
Clay	1.92 \pm 0.0	605 \pm 417
Clay Loam	1.87 \pm 0.23	734 \pm 65
Loam	1.87 \pm 0.09	556 \pm 76
Loamy Sand	1.92 \pm 0.13	317 \pm 313
Sand	1.78 \pm 0.13	221 \pm 112
Sandy Clay Loam	1.90 \pm 0.03	318 \pm 183
Sandy Loam	2.03 \pm 0.13	461 \pm 80
Silt Loam	1.85 \pm 0.04	526 \pm 134
Overall	1.73 \pm 0.60	435 \pm 193

Appendix E. Enrichment Table

Table E.1. Till bank samples individual ER ratios and Particle enriched inorganic P. As we don't have LOI or sequential fractionation on all samples, the averaged till values of 0.9 \pm 0.38% OM and 26 \pm 20 mg/kg OP value was uniformly applied to this table. The values given in thesis text are from individual samples with known values.

Soil ID	Inorganic P with organic P and sand P removed	Particle ER	Particle Enriched Inorganic P on clay/silt (mg/kg)
100	300.61	1.64	493.0004
102	150.72	3.02	455.1744
103	229.84	2.12	487.2608
106	349.89	1.92	671.7888
112	303.86	1.70	516.562
116	325.77	1.63	531.0051
117	396.77	1.78	706.2506
120	265.23	1.63	432.3249

121	308.38	1.84	567.4192
122	270.22	1.78	480.9916
123	345.44	1.57	542.3408
124	261.72	1.53	400.4316
125	379.55	1.67	633.8485
126	201.67	3.85	776.4295
127	478.62	2.13	1019.4606
130	368.49	1.60	589.584
131	360.9	1.05	378.945
135	131.51	3.32	436.6132