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Phosphorus runoff to Clear Creek

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PHOSPHORUS RUNOFF TO CLEAR CREEK

by

Kyla Dean

A thesis submitted in partial fulfillment
of the requirements for the Master of
Science degree in Civil and Environmental Engineering
in the Graduate College of
The University of Iowa

May 2011

Thesis Supervisor: Professor Jerald L. Schnoor

Graduate College
The University of Iowa
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CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

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has been approved by the Examining Committee for the
thesis requirement for the Master of Science degree in
Civil and Environmental Engineering at the May 2011 graduation.

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

Iowa's economy is heavily dependent upon agriculture evident by the 30.75 million acres of farmland composing 86% of total land area in the state (USDA, 2011). Much of this land is devoted to the production of row crops, specifically corn and soybeans, which are the top two agricultural commodities in Iowa (USDA, 2011). In order to achieve high yields of corn and soybeans, nutrients are essential. Increasingly more nitrogen and phosphorus are added to the soil in the form of fertilizer to meet the high crop demands (Hoang et al., 2010). Although the application of fertilizer and use of new technology have greatly helped to increase agricultural production over the past 50 years, it has come at a high cost to water quality (Tesoriero et al. 2009). The transport of nutrients from fertilizer applied on farmlands to waterways is one of the biggest problems affecting watersheds throughout the world (Salvia-Castellvi et al., 2005). This problem is especially significant in Iowa with its abundance of row crop production.

Agriculture's negative effect on water quality is further compounded in Iowa due to the extensive use of subsurface tile drainage. Drainage networks have been implemented in many farms throughout the Midwest to remove excess water (Houser & Richardson, 2010). This is beneficial for crop production but is damaging for water quality since the water flowing through the subsurface drainages is generally loaded with dissolved phosphorus and nitrogen (Royer et al., 2006).

While both phosphorus and nitrogen can be detrimental to water ecosystems, this research focuses on phosphorus in the Clear Creek watershed, which is primarily agricultural, in eastern Iowa. Nitrogen transport and loadings to open waters have been

studied a great deal in the past because the nutrient is extremely mobile (Zaimes & Schultz, 2002). More recently, however, focus has shifted to include the importance of phosphorus entering surface waters (Powlson, 1998). Previously the mobility of phosphorus was not a huge concern because it is readily adsorbed to soil particles but as the importance soil erosion and overland flow as transporters of phosphorus came into light, more focus was shifted towards phosphorus (Powlson, 1998). The excess influx of phosphorus is the leading cause of eutrophication in streams and rivers (Sharpley et al., 1994). Eutrophication in fresh water systems can occur from extremely low concentrations of phosphorus around 10 to 20 $\mu\text{g/L}$ (Heathwaite & Dils, 2000). According to the USEPA (2009), eutrophication is the number one cause of impaired water.

Phosphorus

Phosphorus is an element essential to all living organisms. It helps form the structure of DNA and RNA and plays a vital role in energy storage and transport through ATP and ADP. In row crops, phosphorus is necessary for root development and accelerates plant maturity (Norfleet, 1998). The different forms of phosphorus can be characterized physically and chemically. Physically, phosphorus can be dissolved or particulate. Dissolved phosphorus is defined as phosphorus capable of being passed through a 0.45 μm filter (APHA, 1985). Dissolved (or soluble) phosphorus is primarily composed of orthophosphate which is for used by primary producers (Sharpley et al., 1994). Suspended (or particulate) phosphorus is the remaining phosphorus that is unable to pass through a 0.45 μm filter (APHA, 1985). In water and soil much of the particulate phosphorus consists of dead or living organic matter and phosphorus adsorbed to

particles (Wiederholt & Johnson, 2005). Phosphorus attaches to particles when the negatively charged dissolved phosphorus comes into contact iron, aluminum, calcium, or other cations (Wiederholt & Johnson, 2005). Once attached, the phosphorus in the soil can be liable or nonliable (Troeh & Thompson, 1993). Liable soil phosphorus is loosely bound to the particles and is in equilibrium with surrounding dissolved phosphorus (Zaimes & Schultz, 2002). Dissolved phosphorus that is consumed by plants and other organisms is easily replaced by liable phosphorus. Nonliable phosphorus, however, is tightly bound and will not easily enter solution.

Different forms of phosphorus can also be distinguished chemically. According to the book of *Standard Methods for Examination of Water and Wastewater* (APHA, 1985), there are three forms of phosphorus that can be differentiated chemically: reactive phosphorus, acid-hydrolyzable phosphorus, and organic phosphorus. Reactive phosphorus is the portion of the total phosphorus that reacts with ammonium molybdate and potassium antimonyl tartrate under acid conditions (APHA, 1985). Reactive phosphorus is sometimes referred to as molybdate reactive phosphorus or, incorrectly, as orthophosphate. While reactive phosphorus is largely a measure of orthophosphate, the sulfuric acid in sample preparation can hydrolyze other condensed forms of phosphorus which are then molybdate reactive as well (Zaimes & Schultz, 2002). Acid-hydrolyzable phosphorus is a measure of the remaining inorganic phosphorus that is not a component of the reactive phosphorus. The third form of phosphorus recognized by the book of *Standard Methods* is organic phosphorus which is measured through a perchloric acid digestion method (APHA, 1985).

In agricultural watersheds, like the one studied for this research, the main source of phosphorus from land is agricultural inputs although atmospheric deposition and the soil can also be contributors (Zaimes & Schultz, 2002). Land used for row crop production often covered with fertilizer and/or manure, both of which are sources of phosphorus. Living and decaying plant matter can also contribute phosphorus (Sharpley & Menzel, 1987). Farms with grazing animals add phosphorus through the excretion of feces (Sharpley et al., 1994). In addition to agricultural land use, phosphorus can come from the atmosphere; however, it generally does so in extremely low concentrations (Johnes & Hodgkinson, 1998). Soil acts as a source of phosphorus to watersheds as inorganic phosphorus converts forms through adsorption and desorption (Pierzynski et al., 2000). As previously discussed, adsorption and desorption occur as orthophosphate attaches to and releases from soil particles. Organisms living in the soil can also be phosphorus sources by excreting phosphorus through biological processes, carrying it attached to or within them, and releasing phosphorus when they die (Haygarth & Jarvis, 1999).

Phosphorus can leave the land and enter waterways through the slow pathway of groundwater discharge or more quickly through runoff (Heathwaite et al., 2000). Groundwater discharge is generally not a significant pathway because much of the dissolved phosphorus will adsorb to particles as the water travels through the soil (Tesoriero et al., 2009). The most important phosphorus pathway in a watershed like Clear Creek is runoff. Runoff describes transport due to the slope of the land and includes overland flow, interflow, and tile drainage (Zaimes & Schultz, 2002). Overland flow refers to the flow of water from storm events over the top of the soil when rainfall

intensity overpowers infiltration rates (Johnes & Hodgkinson, 1998). This method of transport contributes significant concentrations of phosphorus to rivers and streams because it is moving the uppermost soil layers which contain the greatest phosphorus concentrations (Haygarth et al., 1998). Although overland flow is capable of moving large masses of phosphorus it is dependent upon rain events to do so. Interflow transport is the shallow, lateral subsurface flow of water in soil. Phosphorus concentrations in interflow are generally low but can make a significant contribution over time (Sharpley & Syers, 1979). The third major pathway for phosphorus to enter water systems in agricultural watershed is through tile drainage networks. Subsurface drainage systems increase the base flow of streams while carrying significant nutrients from the soil (Schilling & Helmers, 2008). One study by Tomer et al. (2010) found that tile intakes can be responsible for transporting about half the total phosphorus load to a stream during a high flow event. The combination of tile drainage and overland flow supply the majority of phosphorus to streams in agricultural watersheds (Tesoriero et al., 2009).

There are sources of phosphorus within streams well. Stream banks with phosphorus attached to solids can contribute phosphorus to the stream through erosion. Sediments in the streambed with attached phosphorus can become resuspended also adding more phosphorus to the water. Once the solids from stream banks or bed become suspended, the phosphorus readily transforms between particulate and dissolved forms through adsorption and desorption reactions (Edwards et al., 2000). Once dissolved, the phosphorus is bioavailable and can be utilized by primary producers (Houser & Richardson, 2010).

Since phosphorus is the limiting nutrient in most rivers and streams (Daniel, et al., 1998), an overabundance of the nutrient can cause unrestricted bacterial and algal growth resulting in eutrophication (Wiederholt et al., 2005). Overly productive eutrophic ecosystems can lead to oxygen depletion in the water as the excess of algae die and are decomposed by bacteria (Zaimes & Schultz, 2002). Algal growth can become so extreme that it will begin to prevent sunlight from penetrating deep into the water (Lee & Lee, 2002). With less sunlight entering, plants are unable to photosynthesize at their regular rate which further reduces available oxygen in the water (SERC, 2005). Eutrophic waters may require more treatment to meet drinking water standards and can cause the water to be restricted for uses such as fishing or recreation which can negatively impact local economies (Zaimes & Schultz, 2002).

The USDA (1997) estimates that agriculture in Iowa is responsible for between 0.3 and 2.0 kg-P/ha-yr of phosphorus in rivers and streams throughout the state. One study by Sharpley and Tunney (2000) compared phosphorus concentrations in surface runoff during a rain event of agricultural land without manure and with manure applied at 50 kg-P/ha and 100 kg-P/ha. The average runoff from the land without manure application was 0.61 mg-P/L while the runoff from the lands with low and high manure application were 1.47 and 2.54 mg-P/L, respectively (Sharpley & Tunney, 2000).

Alberts and Spomer (1985) studied three watersheds where the majority of the land was dedicated to corn production. Over a period of ten years the average dissolved reactive phosphorus transported in overland flow for the three watersheds was 0.381, 0.250, and 0.105 kg/ha. During that same time frame, only 0.031, 0.030, and 0.028 kg/ha were lost through interflow (Alberts & Spomer, 1985). Others have also found that

overland flow is responsible for the largest mass of phosphorus transported to streams while interflow contributes the least and tile drainage contributions are between the two (Sharpley & Syers 1979).

In Tipton Creek in Iowa, which is in an agricultural watershed and is artificially drained with a subsurface tile network, phosphorus concentrations exceeding 1 mg-P/L were measured during eleven rainfall events over a three year period (Tomer et al., 2010). The average annual total phosphorus load over the three year period was 581 g/ha-yr (Tomer et al., 2010).

Objectives

The main objective of this project is to quantify reactive phosphorus runoff to Clear Creek with respect to space and time. The following specific objectives have been established for this research:

1. Determine if the majority of the reactive phosphorus is traveling during base flow or during high flow events.
2. Determine whether more of the reactive phosphorus in Clear Creek is dissolved or associated with solids.
3. Determine the location of sources of reactive phosphorus and whether or not there are any “hotspots.”

To gain a comprehensive understanding of the reactive phosphorus dynamics in the Clear Creek watershed, three different sampling techniques were utilized. Weekly grab samples were collected from three locations throughout the season to see how reactive phosphorus changes over time and to determine how the nutrient loadings change with location, samples were collected from several bridges along Clear on three

different occasions. In addition to the grab samples, automatic samplers were used to collect hourly samples during a storm event to observe how a rainfall event influences reactive phosphorus transport in the watershed.

CHAPTER 2

MATERIALS AND METHODS

All samples collected for analysis came from Clear Creek in Iowa (Figure 2.1). The headwaters of this stream are located in Iowa County while the mouth, which empties into the Iowa River, is in Johnson County of Coralville. The stream is approximately 47 km long and the total area of the Clear Creek watershed is 267 km² (Loperfido, 2009). Within the watershed a majority of the land cover (approximately 85%) is agricultural while the remaining area is forest (8%), roads or urban (6%), and water or barren (1%) (Loperfido, 2009).

Site Description

Three main sites were used for a majority of the sample collection on Clear Creek. The site nearest to the headwaters is located in South Amana at coordinates N41°43'50.00" W91°54'25.41" where samples were collected from the bridge on 190th Street. This location was chosen as a sampling site because flow is measured at this location by a network pressure transducers. A photograph taken from this bridge facing downstream is shown in Figure 2.2. This site is approximately 65.8 km from the mouth of Clear Creek and has a total drainage area of 26.1 km² (Loperfido, 2009). The land cover is mainly row crops of corn, hay, and soy. The stream banks are very steep and highly eroded. Several tile line outlets are visible.

The second sampling site was in Oxford at N41°4'05.50" W91°44'24.93". Samples were collected from the bridge on Eagle Avenue NW. The creek downstream from this bridge is shown in Figure 2.3. This site was chosen for regular sampling because it is the location of a USGS gauging station from which flow data can be

obtained. The Oxford site is 21.9 km from the Iowa River with a drainage area of 151.3 km² (USGS, 2011). The surrounding land cover is composed mainly of row crops and pasture land with some prairie and forest. The stream banks are somewhat steep but much less so than at the Amana site. The Oxford site has two tile lines feeding into Clear Creek.

The third sampling site was further downstream in Coralville with coordinates of N41°40'35.05" W91°35'53.70". Samples were collected from the bridge on Camp Cardinal Road. Like the Oxford site, this site was chosen because it is the location of a USGS steam gauge station. Figure 2.4 shows this site which is 4.5 km from the intersection of Clear Creek with the Iowa River and has a drainage area of 254.1 km² (USGS, 2011). Nearby land use includes forest, prairie land, urban, and industrial. The stream banks are moderately steep but no tile lines are evident.

Sample Collection

Weekly grab samples were collected from the Amana, Oxford, and Coralville sites. A vertical Van Dorn water bottle was lowered from the bridges into the stream to collect the water sample. Upon pulling the water sample up to the bridge the water temperature was measured with a thermometer. The water sample was then poured into a Pyrex bottle and placed in a cooler filled with ice for transport back to the lab. Once in the lab, the water samples were stored at 4° C until they were analyzed.

In addition to the weekly grab samples, on three occasions samples were collected at 12 locations on Clear Creek. The samples were collected where Clear Creek intersects the following roads: 190th Street, Johnson Iowa Road, Black Hawk Avenue, Chambers Avenue, Eagle Avenue, Copi Road, Half Moon Avenue, Ireland Avenue, Jasper Avenue,

340th Street, Camp Cardinal Road, and Highway 6. The 12 sampling locations are shown in Figure 2.5. The samples from these sites were collected and stored in the same manner described for the weekly grab samples.

Samples collected during the storm event were done so using a Teledyne Isco 3700 Portable Samplers. The Isco Samplers were installed at the Amana, Oxford, and Coralville sites. Each sampler was placed on a platform to ensure that it was level and was powered by a deep cycle marine battery. A weighted polypropylene strainer attached to 3/8 inch vinyl suction line was used to draw the water from the stream to the bottles within the sampler by a peristaltic pump. The strainers were hooked to chains that were attached to pipes that had been pounded into the stream bed. The strainers were connected to the chains using zip-ties and were oriented such that the bottom of the strainer was positioned approximately two to four inches above the stream bed. This location was chosen so that it was deep enough to remain fully submerged during low flows but high enough so it would not become filled with sediment from the stream bed. Each sampler contained 24, one liter polypropylene bottles. During the storm event, one 800 mL sample was collected at each site hourly for a duration of 24 hours. At the end of the 24 hour sampling period, the bottles from each site were collected and brought back to the lab. The samples were stored at 4° C until they were analyzed.

Sample Analysis Methods

The turbidity of the samples was determined using a Hach 2100N Turbidimeter. The turbidimeter measures turbidity by directing a beam of light at the sample while a light detector is located 90° to the light source. Light is scattered to the light detector by suspended particles in the sample. A sample with a high density of particles causes more

light to be scattered and the turbidity is a direct function of the amount of light hitting the detector.

Total suspended solids were analyzed using EPA Method 160.2. This technique utilized Millipore AP40 glass fiber disks. The first step of analysis was to prepare the disks. A vacuum filtration apparatus was set up and the filters were washed with three successive 20 mL volumes of distilled water. After being washed, the disk was placed in an aluminum planchet and put in an oven at 105° C for one hour. The disk and planchet were placed in a desiccator to cool, then were weighed to obtain an initial weight.

The washed and weighed disk was placed back in the vacuum filtration apparatus, and a measured portion of the sample was poured through the filter. The size of the sample filtered depended on the turbidity of the sample. Larger portions of clear samples were filtered while highly turbid samples required less of the sample to be filtered. After the sample passed through the filter, the disk was washed with three successive 10 mL portions of distilled water with approximately three minutes between each washing. The disks were placed back in the planchets after filtration and put in the 105°C oven for an hour. Again, after heating the planchets and filters were placed in a desiccator then weighed. The process of heating, desiccating, and weighing was repeated until achieving a change in weight of less than 4% of the previous weight or 0.5 mg, whichever was less. The concentration of TSS in the sample was calculated using the following equation (APHA, 1985):

$$\frac{\text{mg TSS}}{L} = \frac{(\text{final weight, mg} - \text{initial weight, mg}) \times 1000}{\text{sample volume, mL}}$$

Reactive phosphorus was analyzed using the EPA Method 365.3: Colorimetric Ascorbic Acid Method. A combined reagent was made to mix with each sample. The reagent was comprised of the following solutions:

1. Sulfuric acid: 70 mL of 5N H_2SO_4 diluted to 500 mL with distilled water.
2. Potassium antimonyl tartrate solution: 1.3715 g $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}\cdot\frac{1}{2}\text{H}_2\text{O}$ diluted with distilled water to 500 mL.
3. Ammonium molybdate solution: 20 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ dissolved in 500 mL of distilled water.
4. Ascorbic acid: 1.76 g of ascorbic acid dissolved in 100 mL of distilled water. The solution remains stable for 1 week if kept at 4°C

One hundred milliliters of the combined reagent were made using 50 mL sulfuric acid solution, 5 mL potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution. The reagent solution was thoroughly mixed after the addition of each solution. The combined reagent was stable for 4 hours (APHA, 1985).

To prepare the sample for total reactive phosphorus measurement, 1.6 mL of the combined reagent was mixed with 10 mL of the sample. In the presence of acid, the ammonium molybdate and antimony potassium tartrate react with orthophosphates to form an antimony-phospho-molybdate complex. Ascorbic acid then reduces the complex and the solution forms a blue color with an intensity proportional to the orthophosphate concentration. After waiting 10 minutes, but no more than 30 minutes, the absorbance of the solution was measured using a Cary 50 Bio UV-Visible Spectrophotometer at a wavelength of 880 nm with a provided pathlength of 2.5 cm.

To measure dissolved reactive phosphorus the sample needed to be filtered through 0.45 μm membrane filter. While filtration through a 0.45 μm membrane filter is

not a true separation of solids, it is used to make a general separation. The membrane filters were prepared before use to ensure they were free of phosphorus. This preparation was achieved by soaking 50 filters in 2 L of distilled water for 24 hours. After allowing time for the filters to dry, the vacuum filter apparatus was set up and a portion of the sample was filtered through the membrane. Ten milliliters of the filtrate were mixed with 1.6 mL the combined reagent. Again, after 10 minutes of reaction time, but no more than 30 minutes, the absorbance was measured at 880 nm on a spectrophotometer. Suspended reactive phosphorus concentrations were calculated by subtracting the measured dissolved reactive phosphorus from the measured total reactive phosphorus.

$$\text{suspended } P, \text{ mg/L} = \text{total } P, \text{ mg/L} - \text{dissolved } P, \text{ mg/L}$$

Blanks were also prepared and their absorbencies were measured. The blank for dissolved reactive phosphorus was prepared by adding 1.6 mL of the combined reagent to 10 mL of distilled water. The absorbance was measured in the same manner as previously described. Initially the same blanks were used for total reactive phosphorus however the turbidity of the highly turbid samples was interfering with the intensity of the blue color resulting from the antimony-phospho-molybdate complex. The spectrophotometer was measuring the turbidity in addition to color resulting from the phosphorus reaction. In order to correct for this turbidity, different blanks were used for total reactive phosphorus. These blanks were composed of 10 mL of the sample and 1.6 mL of a combined reagent made by mixing together the previously described solutions but excluding the ascorbic acid and potassium antimonyl tartrate. The corrections necessary for highly turbid samples was not realized until after the first several weeks of analysis so total reactive phosphorus and suspended reactive phosphorus measurements

for the first four grab samples are higher than the actual concentrations due to the lack of correction for turbidity.

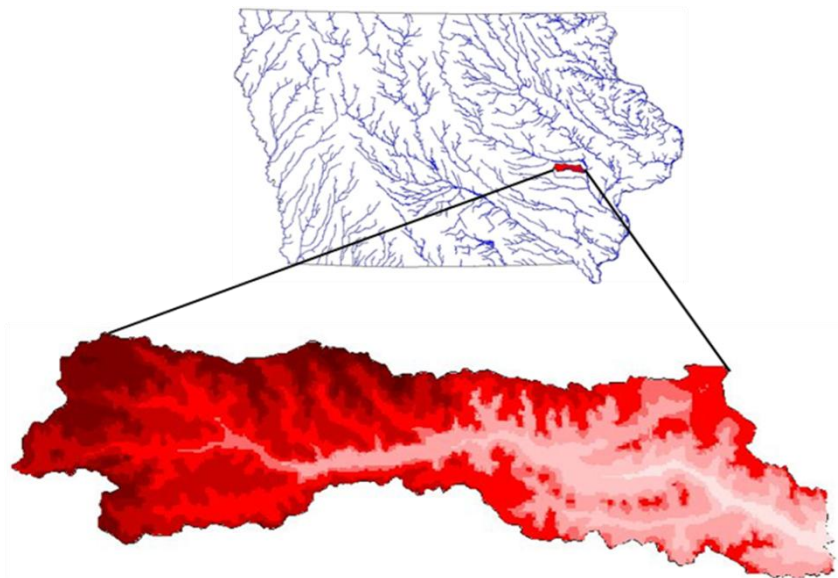


Figure 2.1 Location of the Clear Creek watershed in Iowa and topography of the watershed where darker red areas are more steep than the areas indicated in white (Putney, 2010).



Figure 2.2 Photograph of Clear Creek at the Amana site facing downstream taken July 24, 2010.



Figure 2.3 Photograph of Clear Creek at the Oxford site facing downstream taken July 24, 2010.

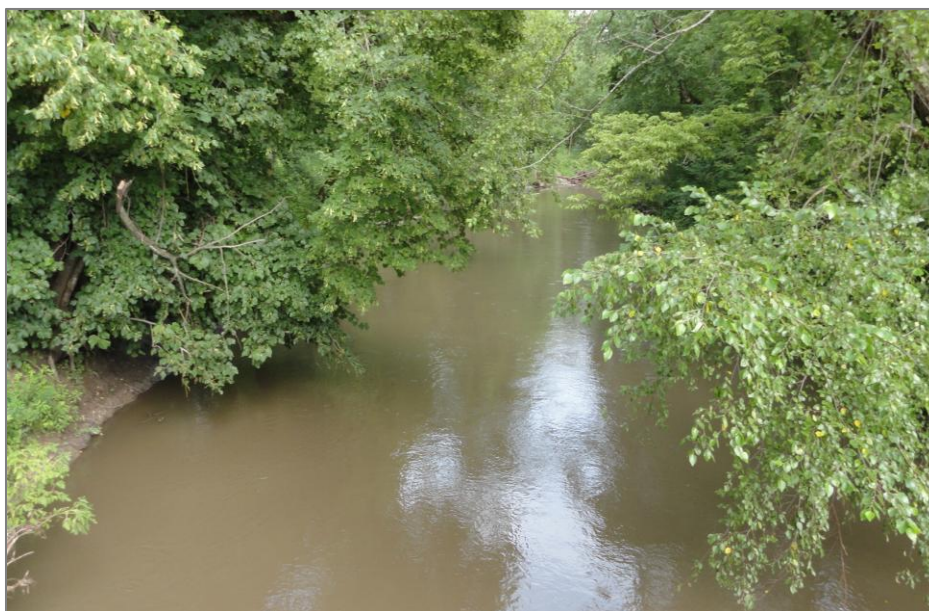


Figure 2.4 Photograph of Clear Creek at the Coralville site facing downstream taken July 24, 2010.



Figure 2.5 Map of the Clear Creek watershed indicating the twelve sampling locations from bridges.

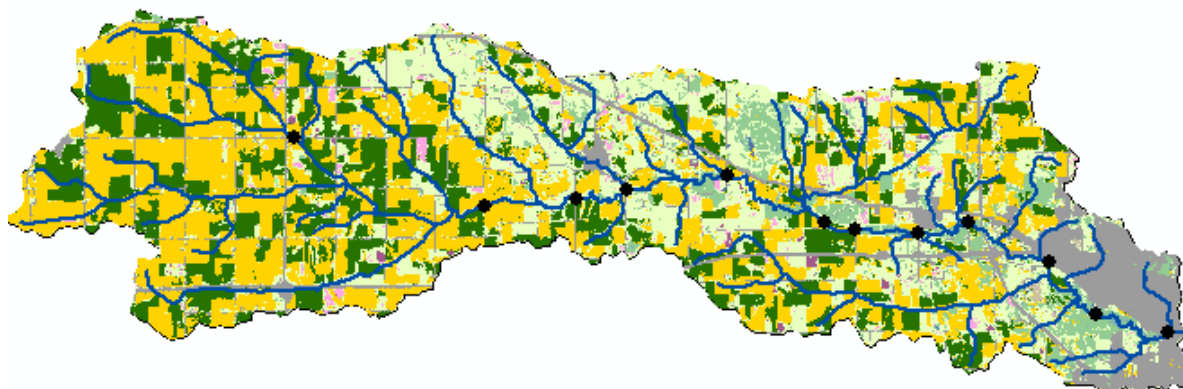


Figure 2.6 Map of the land use in the Clear Creek watershed where yellow and green are corn and soybean, respectively.

CHAPTER 3

RESULTS AND DISCUSSION

Before the reactive phosphorus of any samples could be analyzed, a calibration curve was needed to link measured absorbencies to reactive phosphorus concentrations. A phosphate standard of 1 mg/L was made and diluted to the following concentrations: 0.5 mg/L, 0.1 mg/L, 0.05 mg/L, and 0.01 mg/L. The absorbencies of these standards were measured after being mixed with the reagent and were used to create the calibration curve (Figure 3.1). The high correlation of absorbance and phosphorus concentrations is evident by the strong linear relationship shown in Figure 3.1. This linear trendline was used to calculate the unknown reactive phosphorus concentrations of samples from their measured absorbencies. The equation used is shown below.

$$\text{phosphorus, mg/L} = \frac{\text{measured absorbance} + 0.00324}{0.56477}$$

According to Standard Methods, the ascorbic acid method of phosphorus determination is able to detect concentrations as low as 2 µg/L. The precision of this method was tested by measuring the total reactive phosphorus concentration of one sample ten different times. The average total reactive phosphorus concentration was found to be 0.0978 mg/L with a standard deviation of 0.003 mg/L. The variance of these ten analyses was $9.07 \times 10^{-6} \text{ mg}^2/\text{L}^2$ and the coefficient of variation was 0.0308 mg/L. This indicates that the ascorbic acid method used to determine reactive phosphorus concentrations was very precise.

Weekly Grab Samples

Weekly grab samples collected from the Amana, Oxford, and Coralville sites between June 4, 2010 and December 6, 2010 were analyzed. The flows at each site were also obtained each time a grab sample was collected. Flows at the time of sample collection for the Oxford and Coralville sites were acquired from the USGS website which publishes the 15-minute flows, while daily Amana flows were attained from Athanasios Papanicolaou. The flows at each site during the time of sample collection are shown in Figure 3.2. Throughout the sampling season there were five days when grab samples were collected during high flow; June 16, June 22, June 28, July 6, and September 24. With the exception of these high flow days, Amana flow ranged from 4.6 cfs to 24.7 cfs with an average of 8.5 cfs. During non-storm flow at the Oxford site, the flows ranged from 24 cfs to 100 cfs and the average was 53.4 cfs. Flows at the Coralville site ranged from 40 cfs to 165 cfs and averaged 91 cfs with the exclusion of the five high flow days.

The total, dissolved, and suspended reactive phosphorus concentrations over the sampling time period are provided in Figure 3.3 for Amana, Figure 3.4 for Oxford, and Figure 3.5 for Coralville. It should be noted that all total reactive phosphorus analyses performed on or before June 22, 2010 were done so using only the distilled water blank. Because a sample blank was not used to correct for turbidity, the total reactive phosphorus and suspended reactive phosphorus concentrations are unnaturally high. During normal flow conditions, it is likely that turbidity increased the “measured” total reactive phosphorus by average concentrations of 0.019, 0.040, and 0.043 mg-P/L at the Amana, Oxford, and Coralville sites, respectively. During high flow, turbidity caused the

total reactive phosphorus concentrations to be overestimate by averages of 0.122, 0.469, and 0.607 mg-P/L at the Amana, Oxford, and Coralville sites, respectively. All samples measured after June 22 were corrected for turbidity, making the measurements much more accurate.

Total, dissolved, and suspended reactive phosphorus concentrations measured at the Amana site are shown in Figure 3.3. At this location during normal flow conditions the average total reactive phosphorus concentration was 0.095 mg/L. The average dissolved reactive phosphorus and suspended reactive phosphorus concentrations during normal flow were 0.071 mg/L and 0.024 mg/L, respectively. With the exception of the first five samples where turbidity was not corrected for, the dissolved reactive phosphorus tended to be a larger component of the total reactive phosphorus with suspended reactive phosphorus contributing much less to the total. During high flow conditions dissolved reactive phosphorus was still the major component of total reactive phosphorus but suspended reactive phosphorus was a greater percentage of the total under these conditions than it was during average flow. Total reactive phosphorus was comprised of an average 75% dissolved reactive phosphorus and 25% suspended reactive phosphorus during average flow. Under high flow conditions, dissolved reactive phosphorus was 51% of the total reactive phosphorus while the other 49% consisted of suspended reactive phosphorus.

Reactive phosphorus concentrations of grab samples collected from the Oxford site are displayed in Figure 3.4. Under non-storm flow conditions the average total reactive phosphorus concentration was 0.141 mg/L with a dissolved reactive phosphorus average concentration of 0.085 mg/L and an average suspended reactive phosphorus

concentration of 0.056 mg/L. Similar to the Amana site, total reactive phosphorus was composed of more dissolved reactive phosphorus (which made up 60% of the total) than suspended reactive phosphorus (which was 40% of the total reactive phosphorus) during average flow conditions. During high flow events at Oxford the total reactive phosphorus was only 37% dissolved and 63% suspended. This is reasonable because storms erode soil particles which are associated with particulate phosphorus.

Figure 3.5 shows the total, dissolved, and suspended reactive phosphorus concentrations of grab samples collected from the Coralville site. In Coralville the average total reactive phosphorus concentration was 0.170 mg/L during normal flow. Average dissolved and suspended reactive phosphorus concentrations during normal flow were 0.095 mg/L and 0.075 mg/L respectively. The total reactive phosphorus was 56% dissolved and 44% suspended under low flow conditions. During the high flow events sampled, suspended reactive phosphorus was 77% of the total while dissolved was only 23%.

Total, dissolved, and suspended reactive phosphorus concentrations all increased in the downstream areas of Clear Creek. The Amana site had the lowest concentrations while the Coralville site had the highest concentrations and Oxford was between the two. This is interesting because it means that the headwaters area is not the only contributor of phosphorus. If it was, the phosphorus concentrations would decrease because flow increases downstream which would dilute the phosphorus if there were not additional sources. Because this was not the case and concentrations did increase, it can be deduced that there are additional sources of phosphorus between each site. Furthermore, it has been found that a greater percentage of the total reactive phosphorus entering the water in

the downstream portion of the stream is suspended reactive phosphorus than is in the upstream parts of the stream. Near the headwaters at the Amana site only 25% of the total reactive phosphorus was suspended however closer to the confluence of Clear Creek with the Iowa River at the Coralville site, suspended reactive phosphorus contributed 44% to the total reactive phosphorus. Some of this additional suspended reactive phosphorus can likely be attributed to the higher turbulent waters in the downstream part of the stream stirring up more solids from the streambed. Although the percent of suspended reactive phosphorus increased downstream, the average dissolved reactive phosphorus concentrations were greater than the average suspended reactive phosphorus concentrations at all three sites.

The reactive phosphorus loadings at each site were calculated as a function of concentration and flow (at time of sample collection for Oxford and Coralville and on a daily basis for Amana) using the following equation:

$$\text{load (kg/d)} = \text{concentration (mg/L)} \times \text{flow(ft}^3/\text{s)} \times 86400(\text{s/d}) \\ \times 28.31685(\text{L/ft}^3) \times 10^{-6}(\text{kg/mg})$$

The reactive phosphorus loadings at the Amana, Oxford, and Coralville sites are shown in Figure 3.6, Figure 3.7, and Figure 3.8, respectively. The high flow events in June and the one in September can clearly be seen on the loading graphs. Similar to the reactive phosphorus concentrations, the reactive phosphorus loadings increase downstream. At the Amana site, average normal flow total reactive phosphorus loading of 2 kg/d was measured with a peak of 302 kg/d measured on September 24, 2010. The average flow total reactive phosphorus at Oxford was 20 kg/d and the maximum was 1759 kg/d.

During normal flow at the Coralville site, average total reactive phosphorus was 40 kg/d and the peak was 2439 kg/d.

The loadings show more clearly that much of the phosphorus enters Clear Creek downstream. During average flow conditions the average total reactive phosphorus loading at Oxford is 10 times that of Amana while the average loading at Coralville is 20 times that of Amana. The differences in these concentrations are much lower during the highest flow event on September 24 where Oxford concentrations were just under 6 times that of Amana and Coralville concentrations were just over 8 times higher than Amana.

This could indicate that much more of the phosphorus is coming from an area closer to the headwaters during storm events than during average flow conditions. On the other hand, the smaller difference in reactive phosphorus loadings during the high flow event could be a function of when and where the rain fell and the times and places where samples were collected. For example, if a substantial amount of precipitation fell in the Amana area while very little reached the other two sites, it would be expected that the area near the headwaters would have contributed more phosphorus than usual while the other two sites did not experience such a great increase. The time of grab sample collection relative to the storm could also influence the difference due to the travel time of the water in Clear Creek. If the grab samples were collected shortly after the storm began, the water near Amana carrying the additional phosphorus runoff from rainfall may not have had enough time to flow to Oxford and Coralville before samples were collected at these locations. Weekly samples were not frequent enough to capture the essence of the hydrograph at each location.

In order to better understand why Oxford and Coralville contribute less reactive phosphorus (relative to Amana) during high flow events, it is useful to consider grab samples collected during another high flow event. The next largest reactive phosphorus loading was measured on June 6. On this date, total reactive phosphorus loading at Oxford was approximately 9.5 times that of Amana and at Coralville it was almost 18 times the loading at Amana. These relative numbers are much closer to those found during non-storm flow (recall 10 times Oxford and 20 times at Coralville) indicating that location and time of rainfall greatly influence the reactive phosphorus concentrations measured in the weekly grab samples.

The mass of reactive phosphorus that traveled through Clear Creek over the entire season was estimated using an average Riemann sums form of integration. In order to accomplish this mass sum, the average reactive phosphorus load of two consecutive grab samples was calculated and multiplied by the amount of time between the two samples. After this product was calculated for all grab samples, they were added up to get the total mass transferred between June 4 and November 29. At the Amana site an estimated 4.37 metric tons of total reactive phosphorus, 2.66 metric tons of dissolved reactive phosphorus, and 1.71 metric tons of suspended reactive phosphorus were carried in Clear Creek. The estimated masses of total, dissolved, and suspended reactive phosphorus that passed through the Oxford site were 29.5, 12.4, and 17.1 metric tons, respectively. The total reactive phosphorus that traveled past the Coralville site was estimated to be 49.6 metric tons with 13.2 metric tons of dissolved reactive phosphorus and 36.4 metric tons of suspended reactive phosphorus.

Table 1 summarizes the total mass transport of the three forms of phosphorus per hectare of drainage area at each site throughout the sampling season. The average mass of total reactive phosphorus measured in the Clear Creek Watershed was 1.86 kg/ha while the average dissolved reactive phosphorus mass was 0.79 kg/ha and suspended reactive phosphorus was 1.07 kg/ha. The average total reactive phosphorus measured in Clear Creek was more than three times the annual mass of total reactive phosphorus measured in Tipton Creek, another agricultural watershed in Iowa (Tomer et al., 2010). Masses measured in Clear Creek were within the range of 0.3 to 2.0 kg/ha estimated by the USDA.

The monetary worth of the mass of total reactive phosphorus in the stream was calculated using 2010 fertilizer costs from the USDA (2010). In 2010, fertilizer cost \$1.727/lb as P or \$3808.42/metric ton as P. Using this cost, the values of the total reactive phosphorus washed downstream past the Amana, Oxford, and Coralville sites from June 4 through November 29 were approximately \$16,630, \$112,300, and \$188,900 respectively.

These approximated masses are very rough estimations. The reactive phosphorus loading graphs show how greatly the reactive phosphorus transport increases during storm events which greatly affects the seasonal reactive phosphorus estimation. Because the time between grab samples ranged from 5 to 11 days, it was very possible that entire storm events were missed which would mean the reactive phosphorus for the season was underestimated. It is also possible that what appeared to be continuous high flow conditions like June 16 through July 6 were really only a few storm events that happened to coincide with grab sample collection. While it looks as if there was a continual high

reactive phosphorus flux, in reality there may have been times of low flow and reactive phosphorus concentrations that were missed. This would cause the seasonal reactive phosphorus transport to be overestimated. Because of all these different circumstances that might have been missed during the time between grab samples the calculated reactive phosphorus during the sampling season is only a rough approximation. If flow and reactive phosphorus concentrations are positively correlated, the reactive phosphorus loadings were underestimated. More frequent sampling would be necessary to improve the estimate.

Turbidity and total suspended solid concentrations measured at each site are shown in Figure 3.9, Figure 3.10, and Figure 3.11. Similar to the reactive phosphorus, both turbidity and TSS greatly increased during high flow events and both increased downstream. Average flow turbidities ranged from 11.1 NTU at Amana to 27.9 at NTU at Coralville and average TSS concentrations ranged from 19 mg/L at Amana to 39 mg/L at Coralville. The enormous increase in suspended particles during high flow events was expected as a result of agricultural runoff and additional sediment being stirred up from the streambed and eroded from the bank.

The solids loading for the season is shown in Figure 3.12. The total mass of solids for the entire season was calculated using the Riemann sums method previously described. The TSS that traveled past the Amana site from June 16 to September 29 was estimated to be 1,330 metric tons while 22,200 metric tons were estimated for the Oxford site and 43,400 metric tons estimated for the Coralville site. The mass of solids was also estimated per drainage area and found to be approximately 500, 1,500, and 1,700 kg/ha at the Amana, Oxford, and Coralville sites, respectively.

Turbidity and TSS of the grab samples at all three sites were graphed on opposite axes in Figure 3.13 to determine the relationship between the two attributes. A linear best fit line was placed through the points to come up with the following equation for the relationship:

$$TSS (mg/L) = 1.066 \times turbidity (NTU) + 20.938$$

The R^2 value indicates that with this equation the turbidity accounts for 97% of the variability of TSS. This relationship for solids in Clear Creek can be extremely useful since it is much easier to measure turbidity than TSS.

The relationship between total reactive phosphorus and total suspended solids was determined by graphing the two on opposite axes in Figure 3.14. The relationship between suspended reactive phosphorus and total suspended solids was determined the same way in Figure 3.15. Using these relationships, it was found that TSS accounts for 83% of the variability of total reactive phosphorus and 81% of the suspended reactive phosphorus variability. It was expected that TSS and suspended reactive phosphorus would be highly correlated and that TSS and total reactive phosphorus would also be correlated but not to such an extent. Surprisingly, TSS accounted for more of the total reactive phosphorus variability than the suspended reactive phosphorus variability. This indicates the significant influence of local equilibrium on the forms of phosphorus. The high correlation between total reactive phosphorus and total suspended solids reveals that much of the phosphorus entering the stream is associated with solids but once it is in the stream some of the phosphorus becomes dissolved to achieve local equilibrium within the water.

Water temperature was measured at the time of each grab sample collection and is graphed in Figure 3.16. The grab sample temperatures from the three sites ranged from 62 °F to 81 °F between June and August. After August, temperatures began to drastically drop reaching a minimum of 32 °F on December 6. Throughout the entire season temperatures at each site on any given date were within 7 °F of each other. At the beginning of the season Coralville tended to have the highest temperatures while Amana was often the lowest. Towards the end of the season the trend was opposite; Amana had the highest temperatures while Coralville had the lowest.

Twelve Bridges

The weekly grab samples provided data on how reactive phosphorus in Clear Creek changed over time but the three sampling sites did not provide enough data to fully understand how reactive phosphorus changes with respect to location on Clear Creek. In order to better understand the relationship between reactive phosphorus and location in Clear Creek, samples were collected from several locations in a single day. This was done three times during the sampling season. The first time was May 27 when samples were collected from eight different bridges passing over Clear Creek. Later, four more bridges on Clear Creek were located leading to twelve sampling sites for July 12 and August 21. The reactive phosphorus concentrations with respect to the distance from the confluence of Clear Creek and the Iowa River for each of the three dates are shown in Figure 3.17, Figure 3.18, and Figure 3.19.

The total and suspended reactive phosphorus concentrations appeared the highest during the first sampling set on May 27. This, however, may not be accurate because the total reactive phosphorus at this time was measured using a distilled water blank instead

of the sample blank as previously mentioned which would lead to unnaturally high total and suspended reactive phosphorus concentrations. The dissolved reactive phosphorus, which did not require a sample blank, was somewhat higher during the first sampling set than it was later in the season. Because of this, it is possible that despite total and suspended reactive phosphorus likely being over estimated, the concentrations of these two forms of reactive phosphorus may have actually been higher during the first sampling set than the subsequent two (although not as high as measured). The May sampling also appears to indicate that suspended reactive phosphorus contributes more than dissolved reactive phosphorus to the total reactive phosphorus concentrations. Again, it is unknown whether or not this was actually the case because at this time the analysis methods were not correcting for turbidity of the samples. Overall, the reactive phosphorus concentrations tended to increase as the sampling location approach the confluence of Clear Creek with the Iowa River.

In July, much lower total and suspended reactive phosphorus concentrations were measured. This was partly due to the analysis method that corrected for turbidity. The dissolved reactive phosphorus concentrations measured in July were somewhat less than the concentrations in May but at any location the difference in dissolved reactive phosphorus between the two dates was less than 0.060 mg/L. As a general trend, both total and dissolved reactive phosphorus concentrations increased as the sampling location approached the Iowa River. Suspended reactive phosphorus concentrations seemed to increase from the headwaters until about 10 miles from the mouth of Clear Creek where the concentrations continually decreased. On average, dissolved reactive phosphorus was a larger contributor than suspended reactive phosphorus to total reactive phosphorus on

this date. The total reactive phosphorus was comprised of about 66% dissolved and 34% suspended.

The third and final sampling of the twelve bridges was conducted on September 21. Total reactive phosphorus concentrations were measured for all locations but dissolved reactive phosphorus was not measured at the Amana, Oxford, and Coralville locations because the samples were accidentally discarded. Since dissolved reactive phosphorus wasn't measured, it was not possible to determine the suspended reactive phosphorus at these locations either. The average concentrations of the three forms of reactive phosphorus were all higher in September than June. On this date dissolved reactive phosphorus was responsible for about 61% of the total reactive phosphorus while suspended reactive phosphorus contributed the other 39%. All forms of reactive phosphorus tended to increase as the sampling location approached the confluence of Clear Creek with the Iowa River. In September the increase in reactive phosphorus concentrations as a function of location was fairly linear. By adding a best fit line in Figure 3.20, it was determined that location accounted for 97% of the variability of total reactive phosphorus, 85% of the variability of dissolved reactive phosphorus, and 66% of the variability of suspended reactive phosphorus. This clearly indicates a high correlation between total reactive phosphorus concentration and sampling location.

The turbidity and TSS of the samples collected July 12 are shown in Figure 3.21. The lowest turbidity and TSS concentration were measured closest to the headwaters at the Amana location. Both attributes gradually increased as the sampling location approached the Iowa River until peaking at the Coralville location. At the Highway 6

location both turbidity and TSS greatly decreased possible due to sedimentation of particulate material as the stream widened.

Temperature was also measured at all sampling locations on July 12 and is shown in Figure 3.22. As with the other characteristics the temperature tended to increase from the headwaters toward the confluence of Clear Creek with the Iowa River. Although this could be attributed to stream properties, it is also possible that it was a result of the time of day when the sample was collected. The first sample was collected at Amana at 11:30 am with the subsequent samples collected in order of location with 10 to 35 minutes elapsing between each collection. The final sample, at Highway 6, was acquired at 2:40 pm. This increase in water temperature could be the result of the sun warming up the water as it gets later in the day. This theory is supported by the temperatures measured at the Amana and Johnson Iowa locations. The greatest time elapsed between these two locations while the greatest temperature change of 2 °F was measured at these locations.

Storm Event

Another objective of this work was to determine if a majority of the reactive phosphorus travelled during high flow events. To better understand phosphorus transport, hourly samples were desired during a storm event. Obtaining these samples was accomplished through the use of an automatic Isco sampler. The goal was to collect hourly samples during several storm events throughout the spring, summer, and fall. This did not happen as planned because of several problems. The plan was to deploy the automatic samplers in early spring so that they would be ready to operate by late spring. The samplers and necessary equipment were ordered in March but did not arrive until June. Once delivered the samplers needed to be set up and programmed. The samplers

were finally taken to the field and set up on June 6. At this time, however, the samplers could not be operated because the land around the stream was so steep that platforms were necessary to level the samplers in order to ensure that the water delivered by the distributor would make it into the correct bottles.

An IIHR employee was contacted to construct platforms for the sampler and one was finished and installed at the Coralville site on July 15. The next two platforms were completed July 26 however several components necessary for installation were missing. Three days later all platforms were set up and samplers were programmed and ready to collect. By this time the rainiest part of the season had passed and storm events were few and far between. Throughout August and September the Isco samplers were triggered three times to sample during storms but each time there was an issue. The first time the strainers had come out of the water and unable to collect the samples. The next time the samplers worked but very little rain fell and no change was noticeable on the hydrographs. The third time the samplers were not receiving power because of an issue with the batteries and connecting cable. Finally, on October 23 the samplers were triggered during a storm and successfully collected samples hourly from 3:00 am through 2:00 am October 24. The storm on October 23 however was a very minor storm compared to the five events caught through grab samples.

The hourly reactive phosphorus concentrations measured during the storm event at Amana, Oxford, and Coralville are shown in Figure 3.23, Figure 3.24, and Figure 3.25. At the Amana site, reactive phosphorus concentrations peaked between 1:00 and 3:00 pm and then again near the end of the sampling period the next day at 1:00 and 2:00 am. Dissolved reactive phosphorus concentrations were generally higher than suspended

however when the highest total concentrations were measured the suspended reactive phosphorus was greater than dissolved. The hourly reactive phosphorus concentrations at Oxford were much lower than those at Amana. Reactive phosphorus concentrations at this location peaked toward the end of the sampling time from about 9:00 pm until the end at 2:00 am but the peak at this site was much smaller than the peak at Amana. At the Coralville site the concentrations were also much lower than those measured at Amana. The peak at Coralville occurred at the end of the sampling set from 11:00 pm to 2:00 am.

Figure 3.26, Figure 3.27, and Figure 3.28 also show the hourly concentrations at each site but all with the same scale on the y-axis. These figures show much more clearly how much higher the reactive phosphorus concentrations were at the Amana site. The peak concentrations at Oxford and Coralville are just barely above the low concentrations at Amana. The reactive phosphorus dynamics during this storm event were much different than the grab samples. Even during high flow events with the grab samples, the reactive phosphorus concentrations increased downstream. Again, this could be a result of sampling time with respect to the time of rainfall. The automatic samplers collected samples just before and at the beginning of a storm. The grab samples were collected after storms so it is possible that toward the beginning of rain events the highest concentrations are at the Amana site while after storm events the highest concentrations are found at the Coralville site.

Total, dissolved, and suspended reactive phosphorus loadings calculated for each site are shown in Figure 3.29, Figure 3.30, and Figure 3.31, respectively. These figures show that despite Amana having the greatest reactive phosphorus concentrations, the loading at this site was the smallest. Reactive phosphorus loading at Oxford was

somewhat larger while the largest mass of reactive phosphorus traveled past Coralville loading. These high loadings at Coralville illustrate how much the flow can impact loadings. The highest flow at Amana during this 24 hour period was 7 cfs while Coralville peaked with 180 cfs. For most of the sampling time there was not a very large difference between dissolved and suspended reactive phosphorus loadings, however in the last few hours the suspended reactive phosphorus loads at Coralville greatly increased. This is likely the time when the storm arrived at the Coralville station causing greatly increased the flow and solids runoff both of which contributed to the high mass flux of suspended reactive phosphorus.

The hourly turbidity and TSS measured at each site are shown in Figure 3.32, Figure 3.33, and Figure 3.34. At the Amana site five of the turbidity and TSS measurements were discarded because of their unnaturally high values due to sampling errors. When these samples were collected from the Isco the bottles were filled over the top and contained a great amount of sediment. The Isco sampler display also indicated that no liquid was detected for these samples. It is probable that during collection of these samples the strainer was at least partially covered with sediment causing inaccurate measurements of the water's turbidity and TSS which is why these samples were left out of Figure 3.32.

The highest turbidity and TSS concentrations were measured at Coralville while the lowest were at Amana. The turbidity and TSS at Amana was high at the beginning of the sampling period then mostly decreased with a small spike towards the end of the 24 hour period. At the Oxford site, turbidity and TSS started out lower with a lot of variability and peaked in the last seven hours of sample collection. Similarly, turbidity

and TSS measured at Coralville were lowest in the beginning with high variability and peaked in the last five hours. The large increases at 8:00 pm and 10:00 pm at Oxford and Coralville, respectively, likely corresponded to the time when the storm arrived at each location. From the reactive phosphorus concentrations, it was estimated that the storm appeared in Amana around 1:00 pm but this cannot be corroborated by the TSS and turbidity since the 2:00 and 3:00 pm samples were discarded as previously mentioned. There was, however, a small peak in TSS at 1:00 pm which could indicate the beginning of higher concentrations.

The solids loadings during the 24 hour sampling period are shown in Figure 3.35. As with the reactive phosphorus, the mass of solids passing through the Amana site was minimal compared to the other two sites. The solids flux at Coralville was usually a bit larger at Coralville than at Oxford until 8:00 pm when the storm arrived at Coralville causing the mass of solids to increase drastically. This was consistent with solids loadings measured in the weekly grab samples.

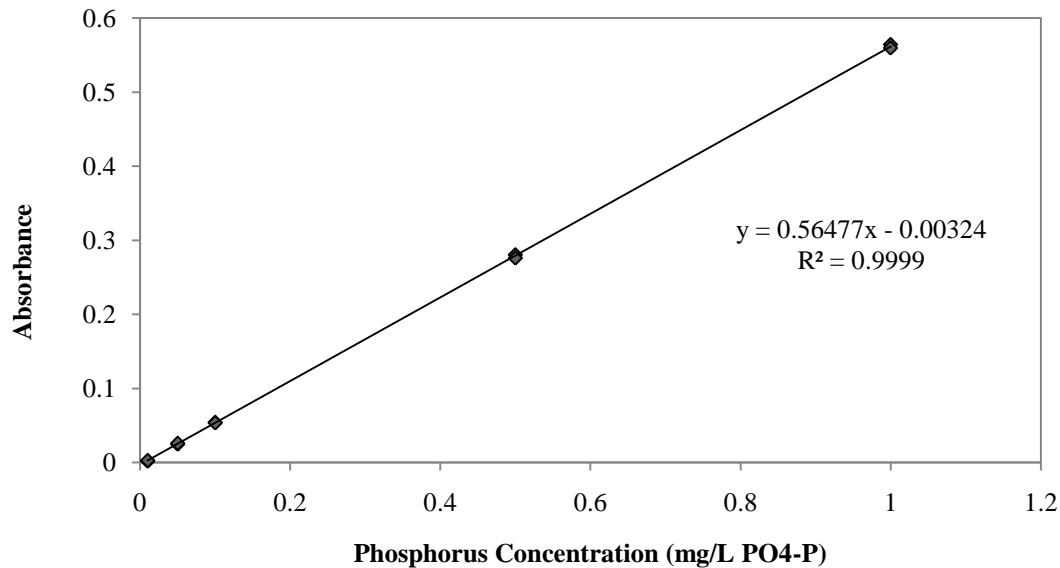


Figure 3.1 Calibration curve for absorbance created using phosphate standards ranging from 0.01 mg-P/L to 1.0 mg-P/L.

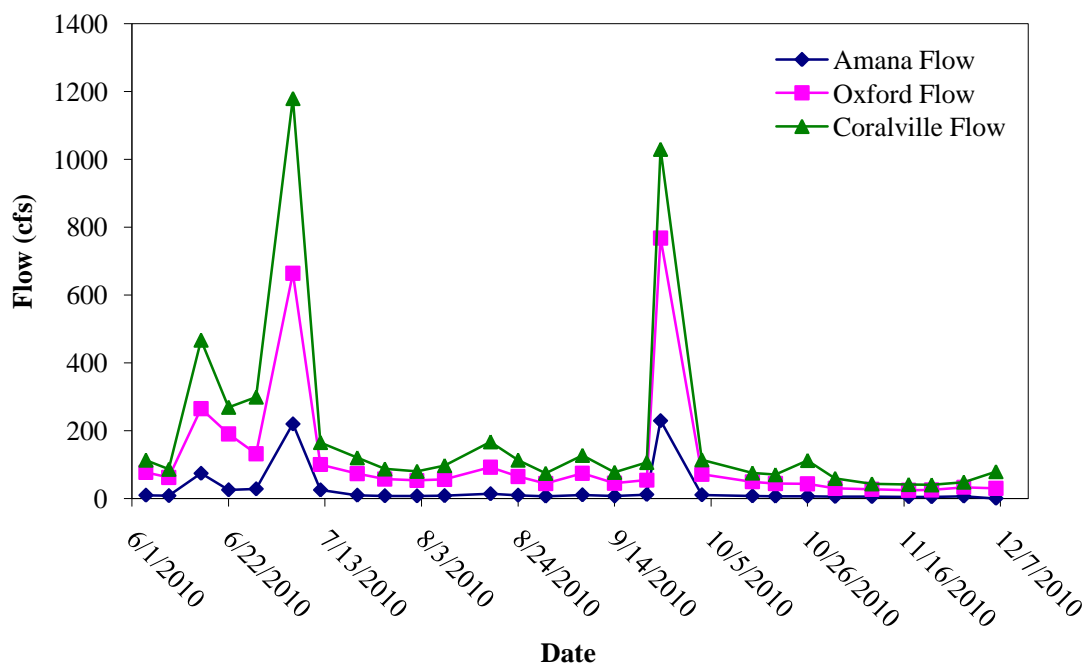


Figure 3.2 Amana, Oxford, and Coralville flows in cfs at time of sample collection throughout sampling season.

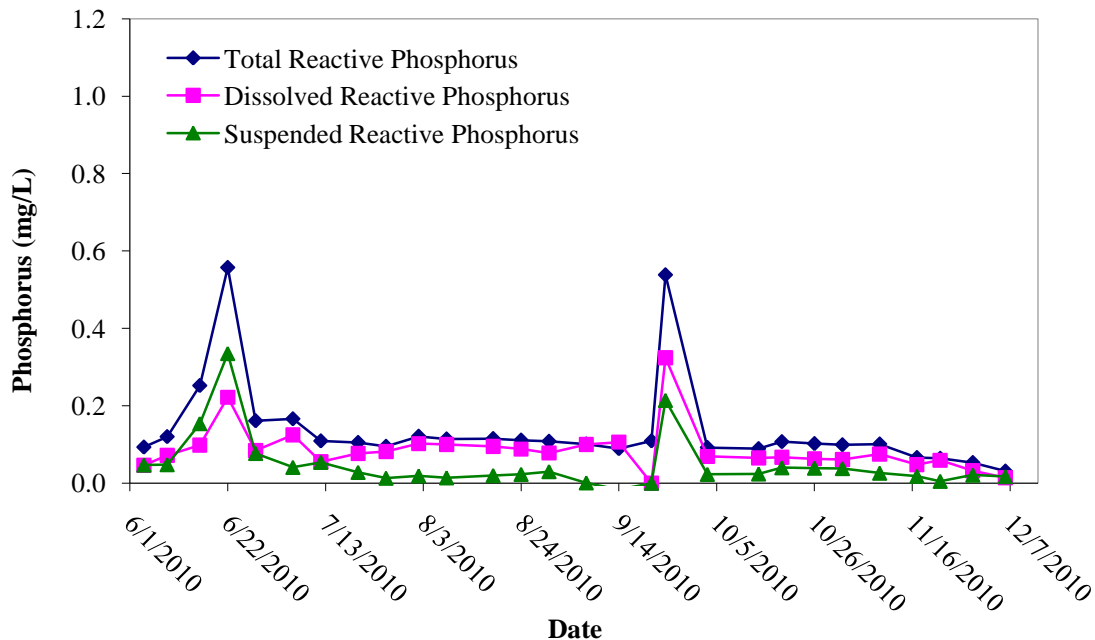


Figure 3.3 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of grab samples at Amana site for entire sampling season.

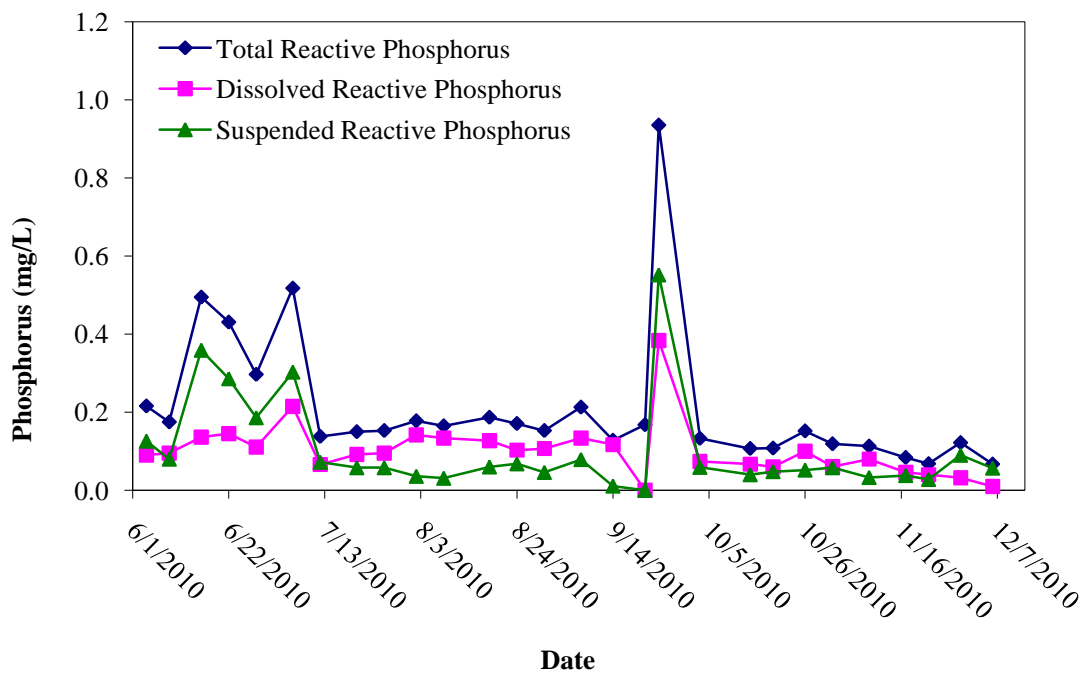


Figure 3.4 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of grab samples at the Oxford site for entire sampling season.

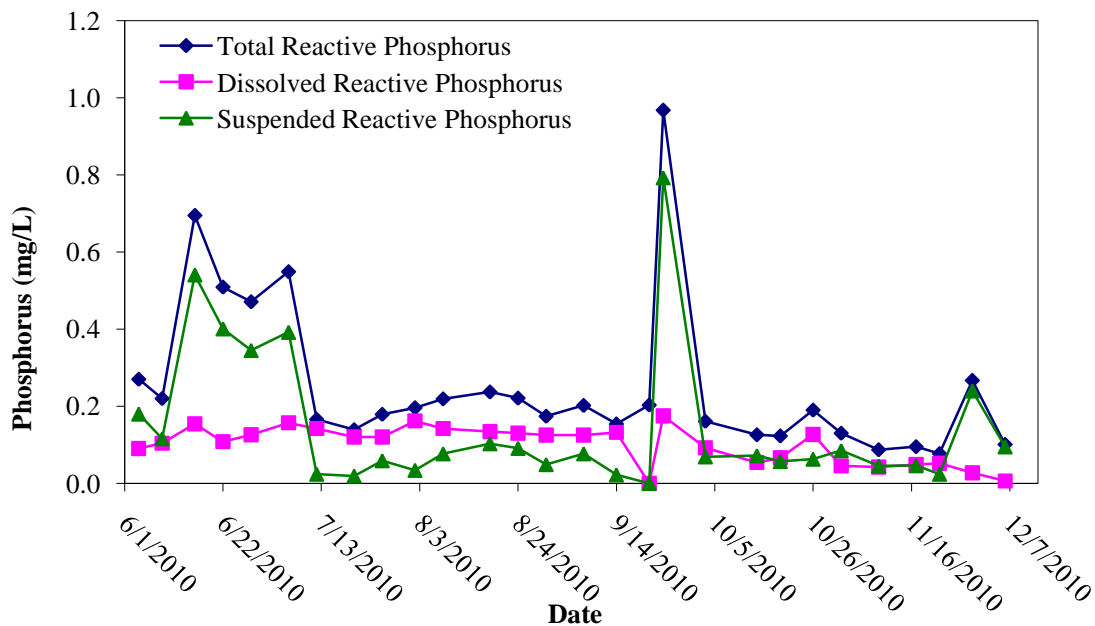


Figure 3.5 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of grab samples at the Coralville site for entire sampling season.

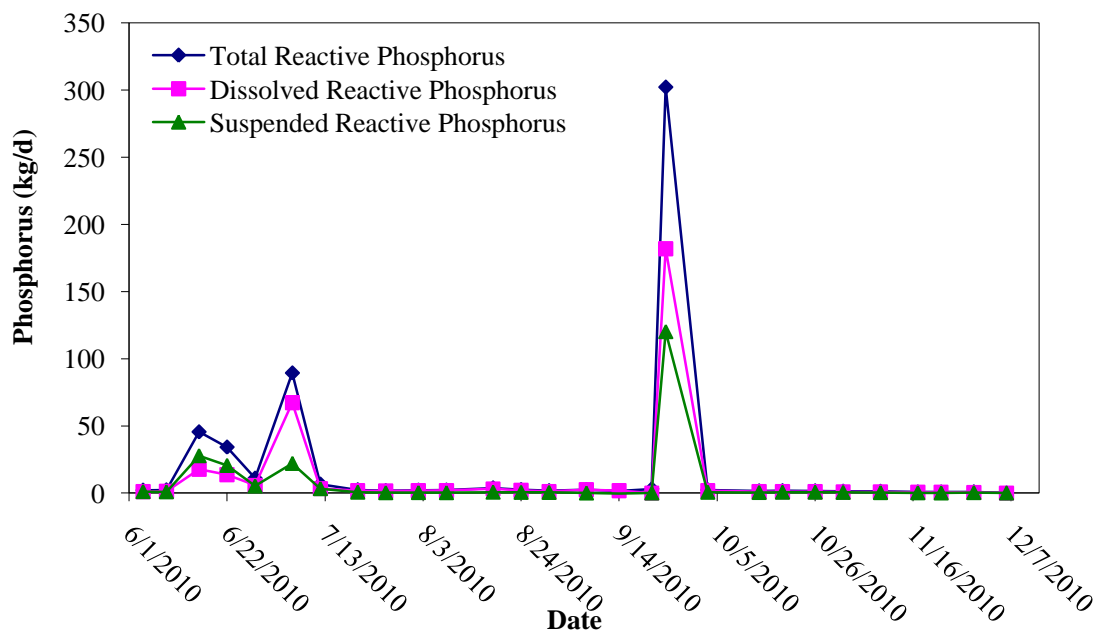


Figure 3.6 Total, dissolved, and suspended reactive phosphorus loadings in kg/d of grab samples at the Amana site for entire sampling season.

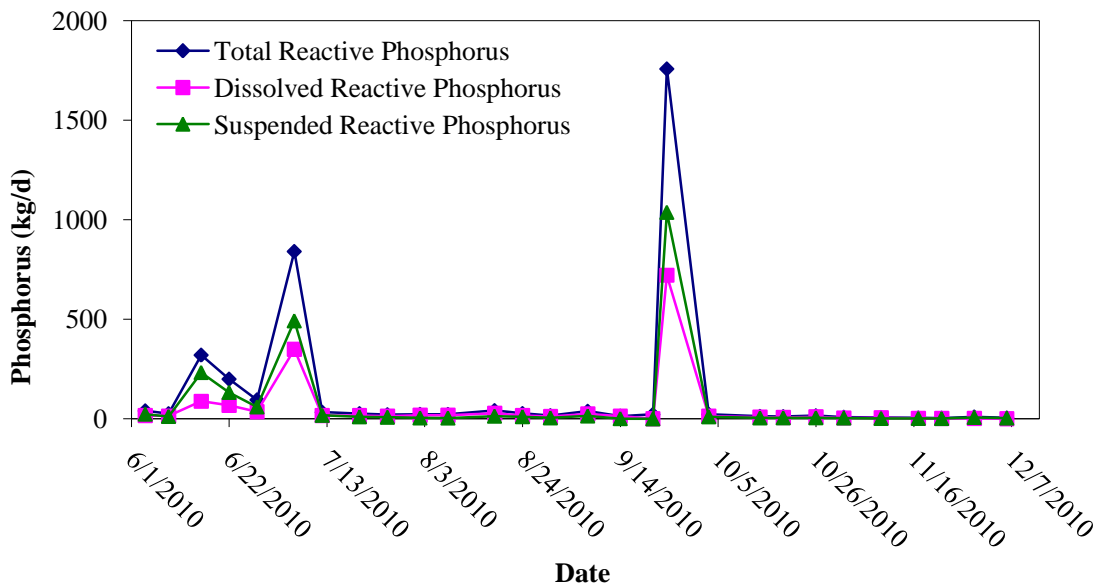


Figure 3.7 Total, dissolved, and suspended reactive phosphorus loadings in kg/d of grab samples at the Oxford site for entire sampling season.

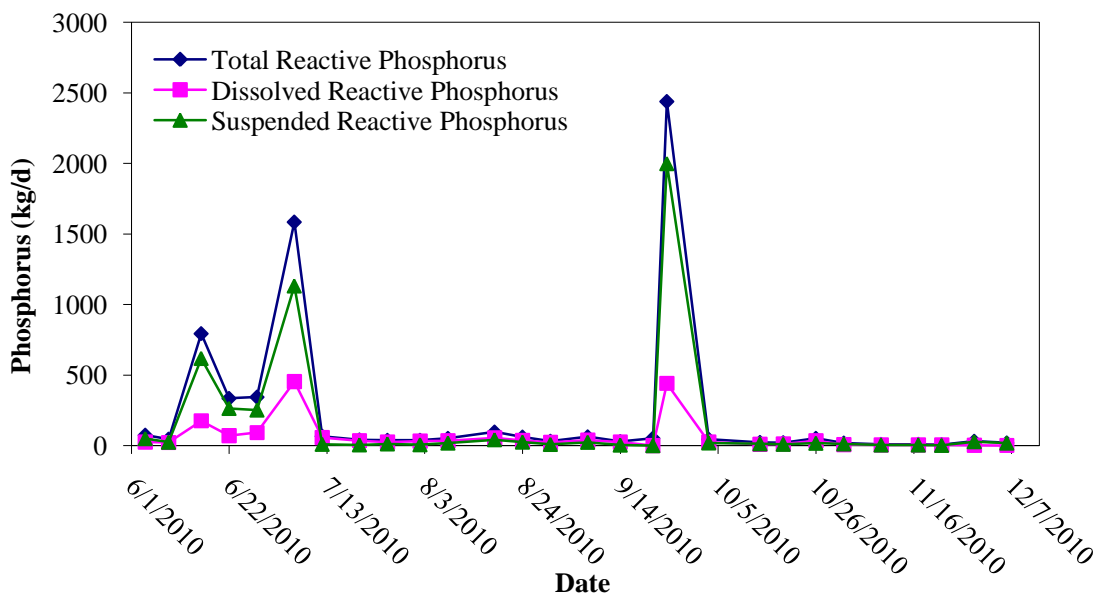


Figure 3.8 Total, dissolved, and suspended reactive phosphorus loadings in kg/d of grab samples at the Coralville site for entire sampling season.

Table 3.1 Masses of total, dissolved, and suspended reactive phosphorus in kg/ha measured at each site from June 4 through November 29.

	Amana Site	Oxford Site	Coralville Site
Total Reactive Phosphorus (kg/ha)	1.67	1.95	1.95
Dissolved Reactive Phosphorus (kg/ha)	1.02	0.82	0.52
Suspended Reactive Phosphorus (kg/ha)	0.65	1.13	1.43

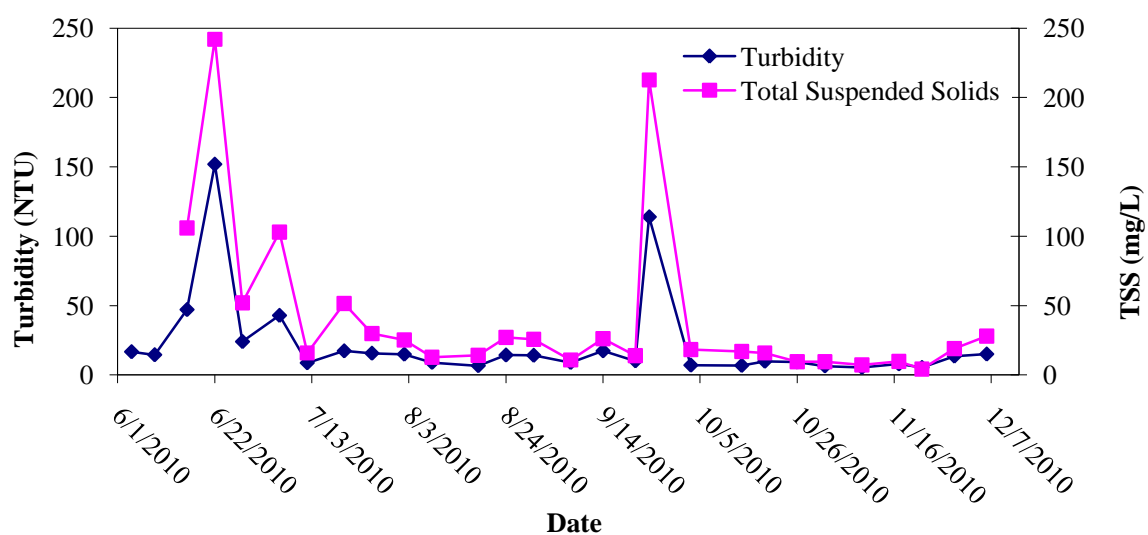


Figure 3.9 Turbidity in NTU and TSS in mg/L of grab samples at the Amana site throughout sampling season.

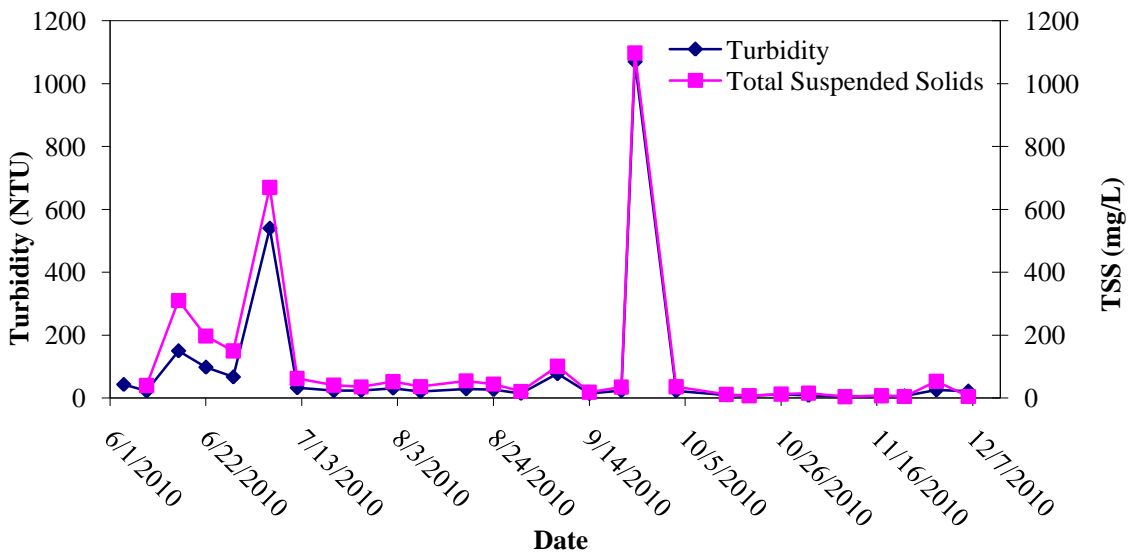


Figure 3.10 Turbidity in NTU and TSS in mg/L of grab samples at the Oxford site throughout sampling season.

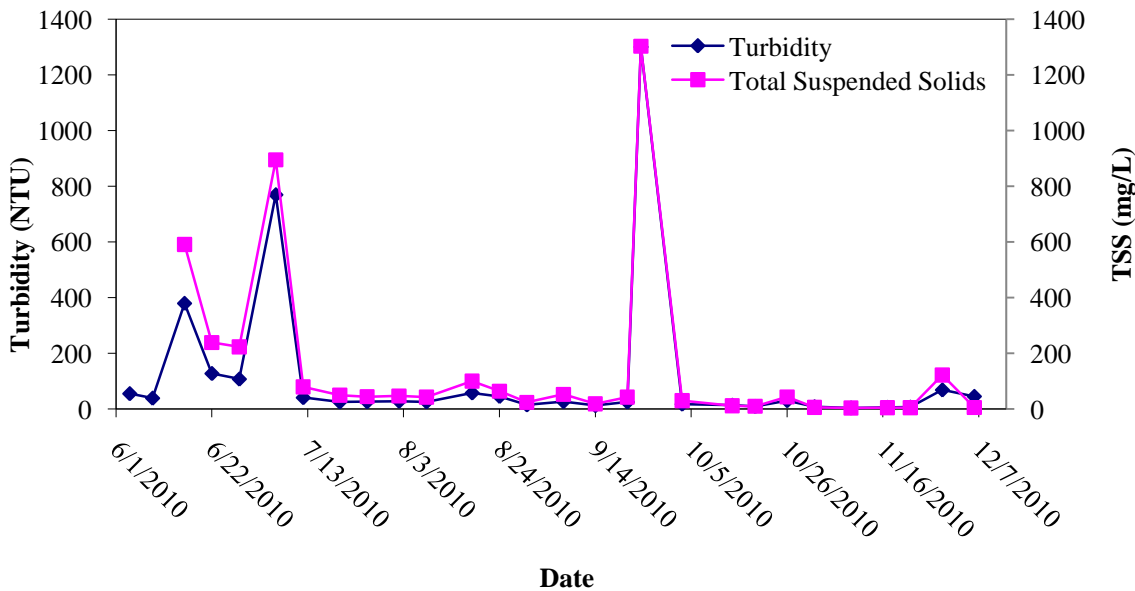


Figure 3.11 Turbidity in NTU and TSS in mg/L of grab samples at the Coralville site throughout sampling season.

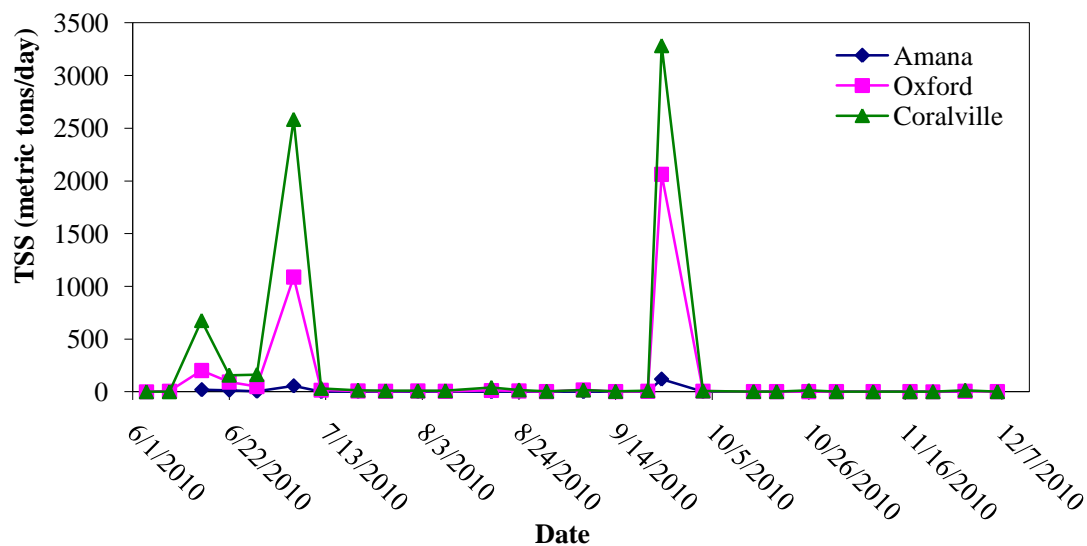


Figure 3.12 Total suspended solids loadings in metric tons/day at Amana, Oxford, and Coralville for the sampling season.

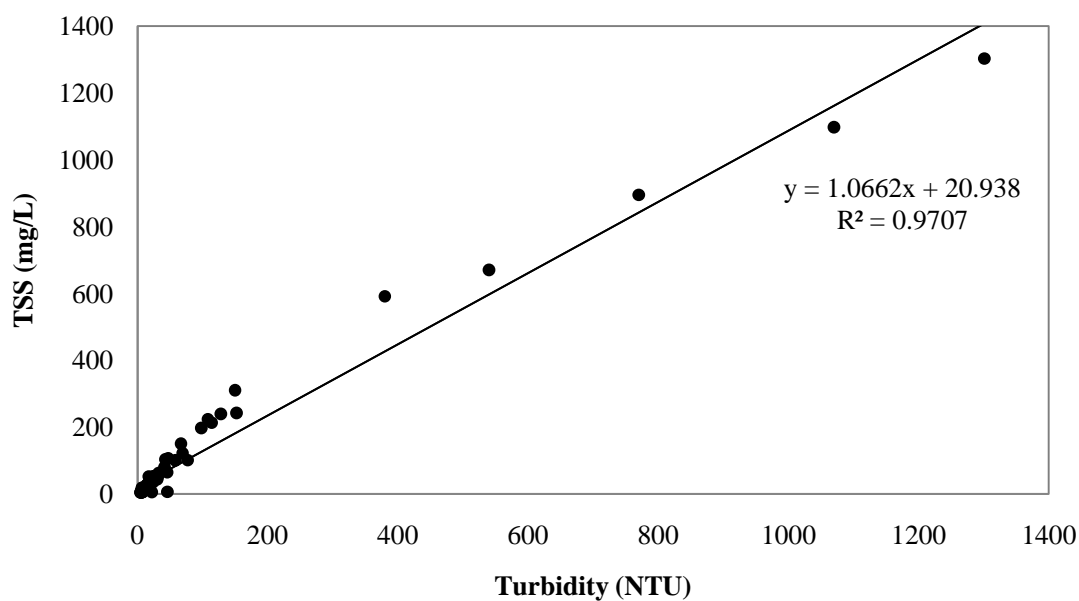


Figure 3.13 TSS (mg/L) and turbidity (NTU) of grab samples at the Amana, Oxford, and Coralville sites throughout entire sampling season. The relationship between the two was determined using a best fit linear regression.

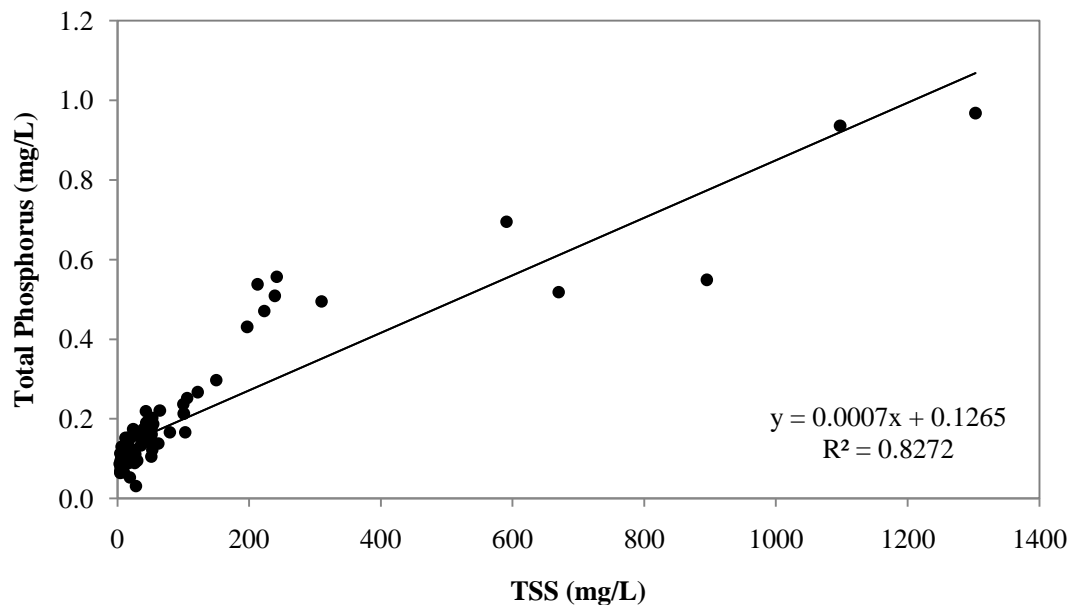


Figure 3.14 Total reactive phosphorus and total suspended solids of grab samples at the Amana, Oxford, and Coralville sites throughout the sampling season. The relationship between the two was determined using a best fit linear regression.

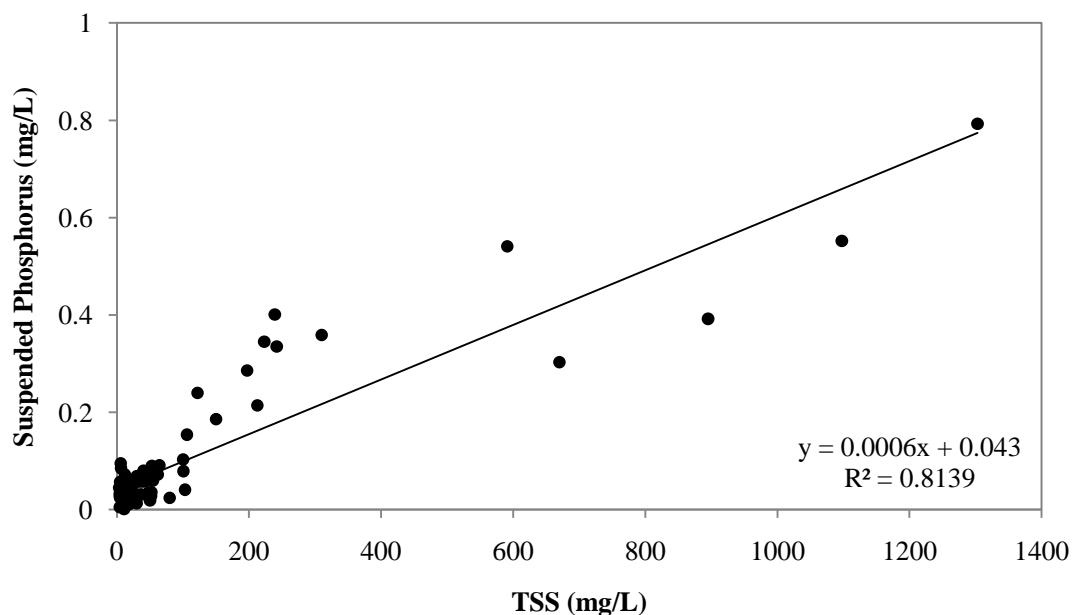


Figure 3.15 Suspended reactive phosphorus and total suspended solids of grab samples at the Amana, Oxford, and Coralville sites throughout the sampling season. The relationship between the two was determined using a best fit linear regression.

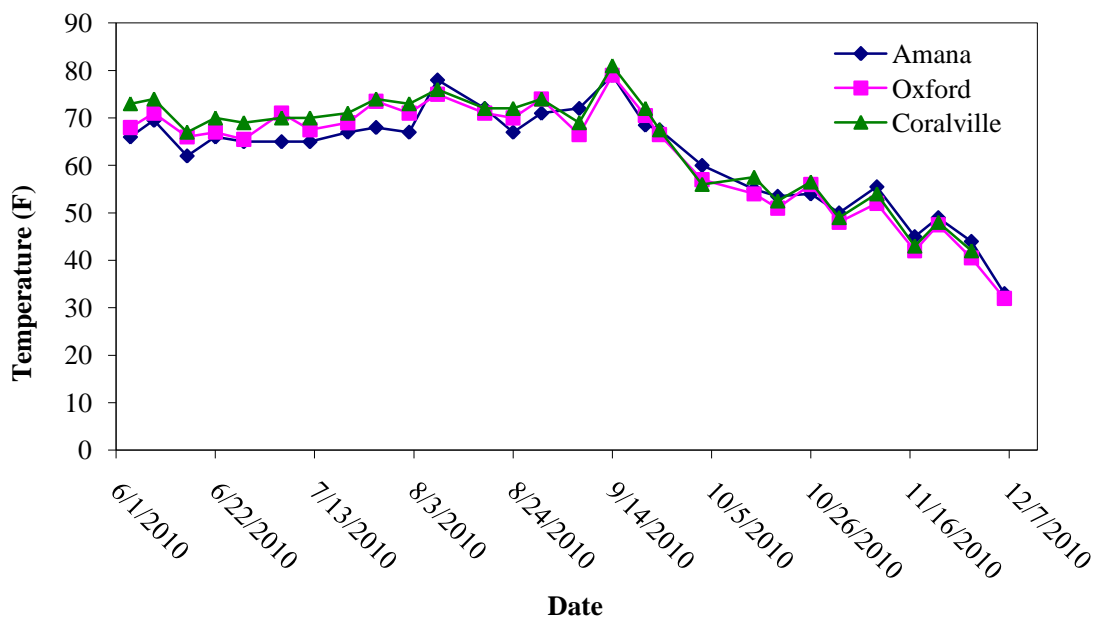


Figure 3.16 Temperature in degrees Fahrenheit at Amana, Oxford, and Coralville sites throughout sampling season.

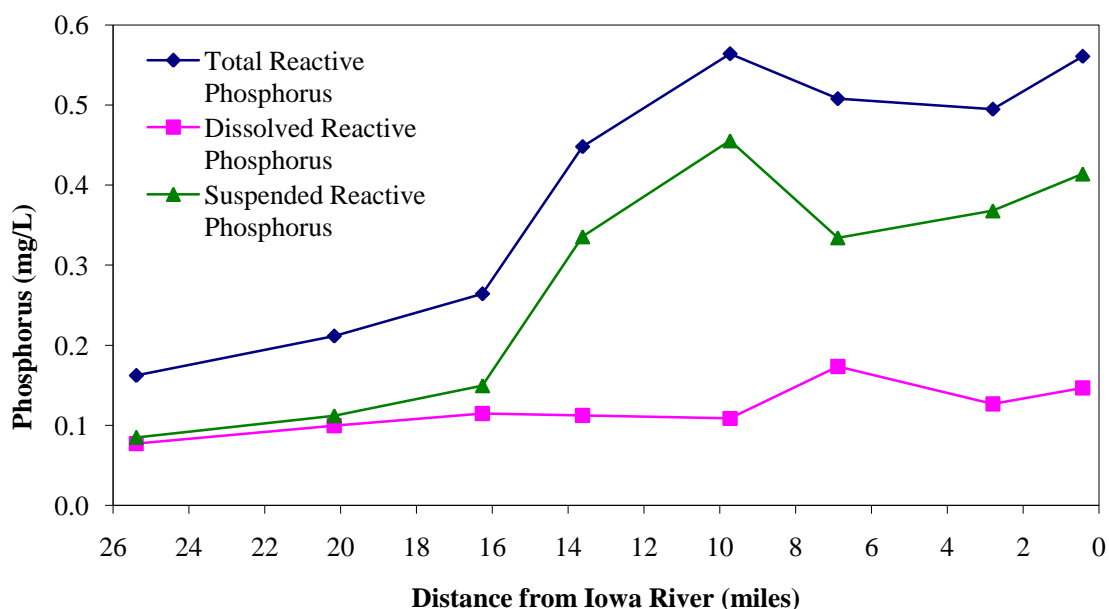


Figure 3.17 Total, dissolved, and suspended reactive phosphorus concentrations as a function of distance from the confluence Clear Creek and the Iowa River measured at 8 locations on May 27.

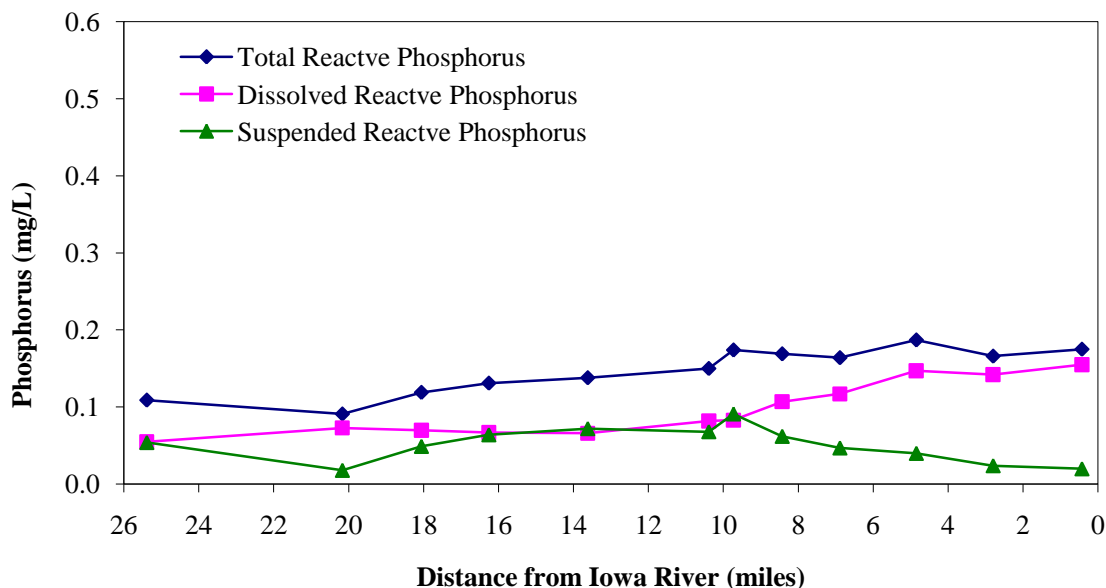


Figure 3.18 Total, dissolved, and suspended reactive phosphorus concentrations as a function of distance from the confluence Clear Creek and the Iowa River measured at 12 locations on July 12.

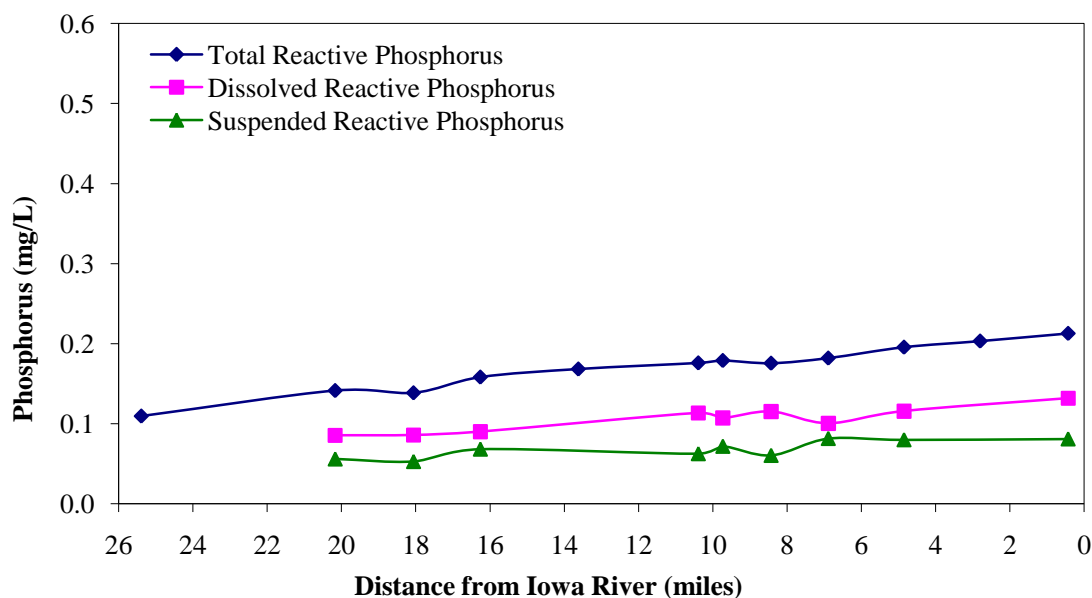


Figure 3.19 Total, dissolved, and suspended reactive phosphorus concentrations as a function of distance from the confluence Clear Creek and the Iowa River on September 21. Total reactive phosphorus was measured at 12 locations while dissolved and suspended reactive phosphorus were determined for 9 locations.

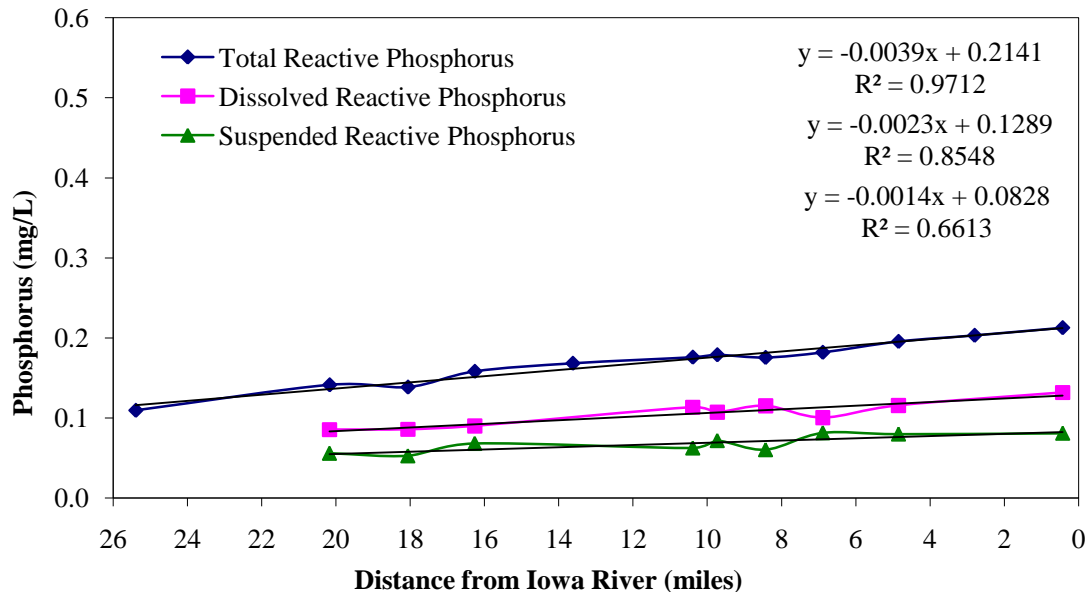


Figure 3.20 Total, dissolved, and suspended reactive phosphorus concentrations as a function of distance from the confluence Clear Creek and the Iowa River on September 21 with linear, best fit trendlines.

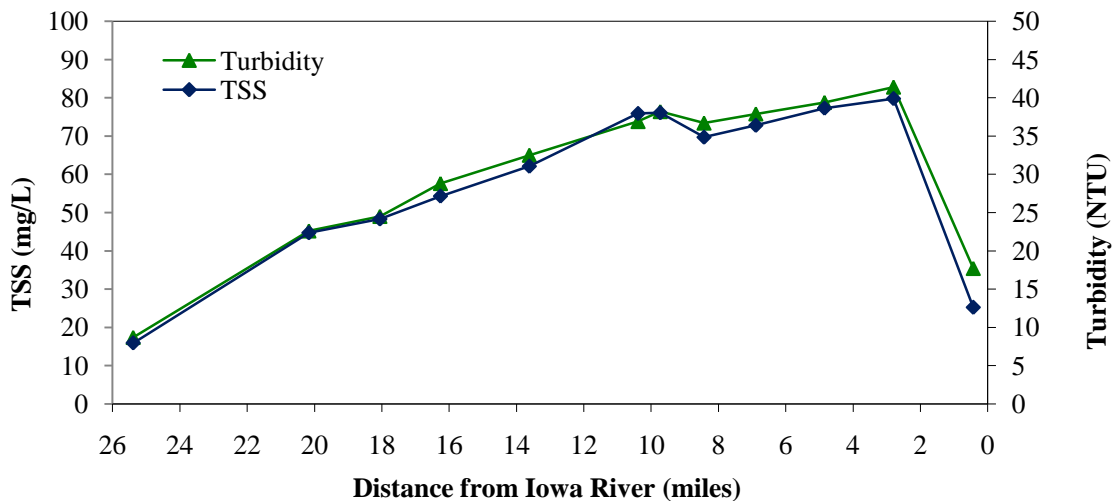


Figure 3.21 Turbidity (NTU) and TSS (mg/L) as a function of distance from the Iowa River at 12 locations sampled on July 12.

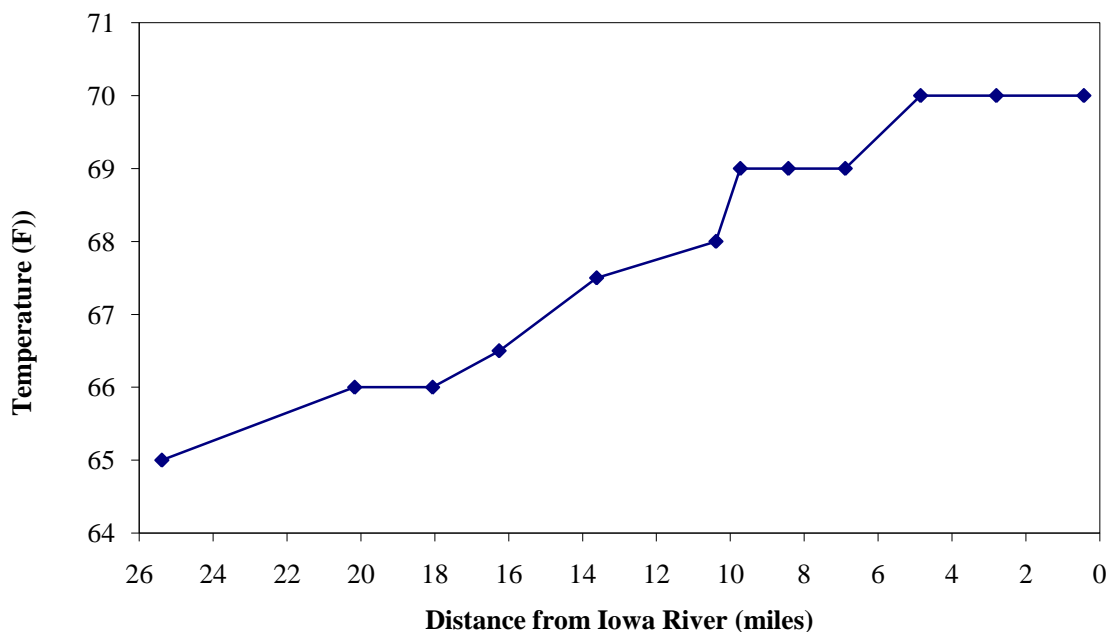


Figure 3.22 Temperature in degrees Fahrenheit as a function of distance from the Iowa River at 12 locations sampled on July 12.

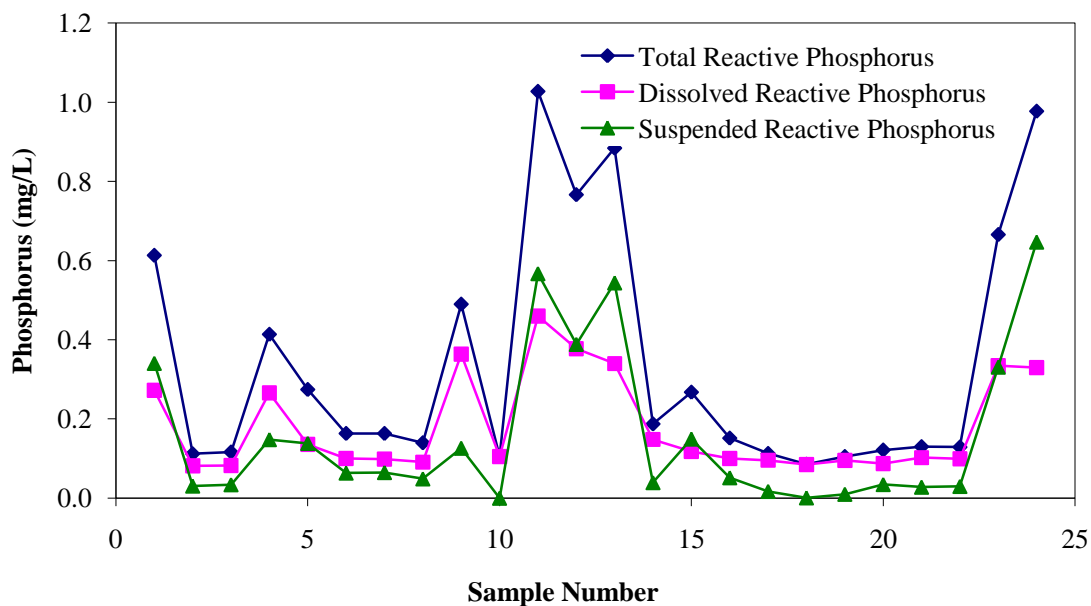


Figure 3.23 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of hourly samples collected at the Amana site using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

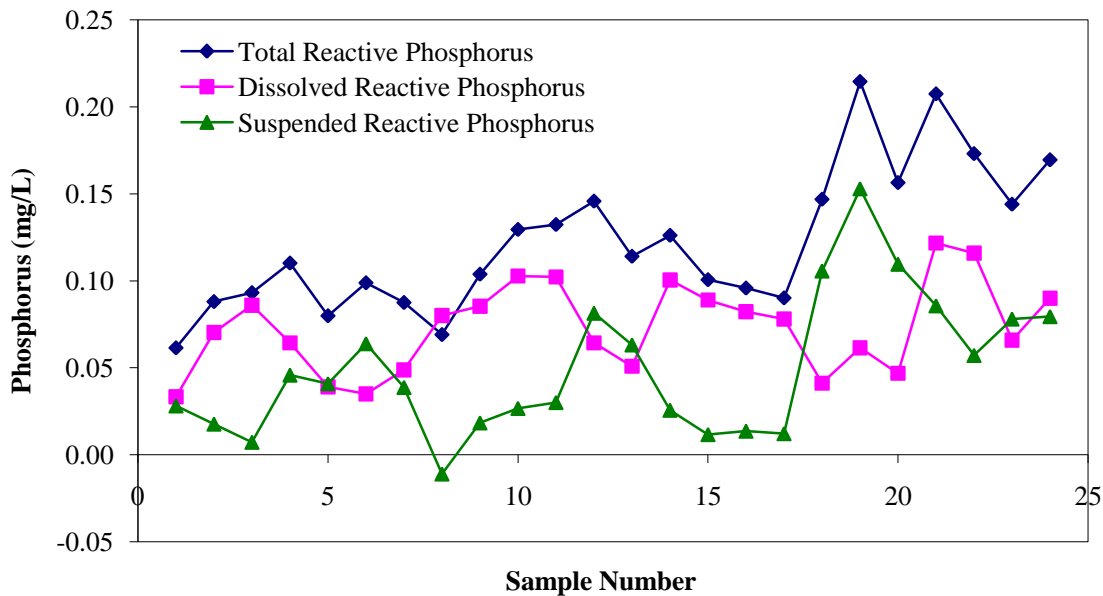


Figure 3.24 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of hourly samples collected at the Oxford site using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

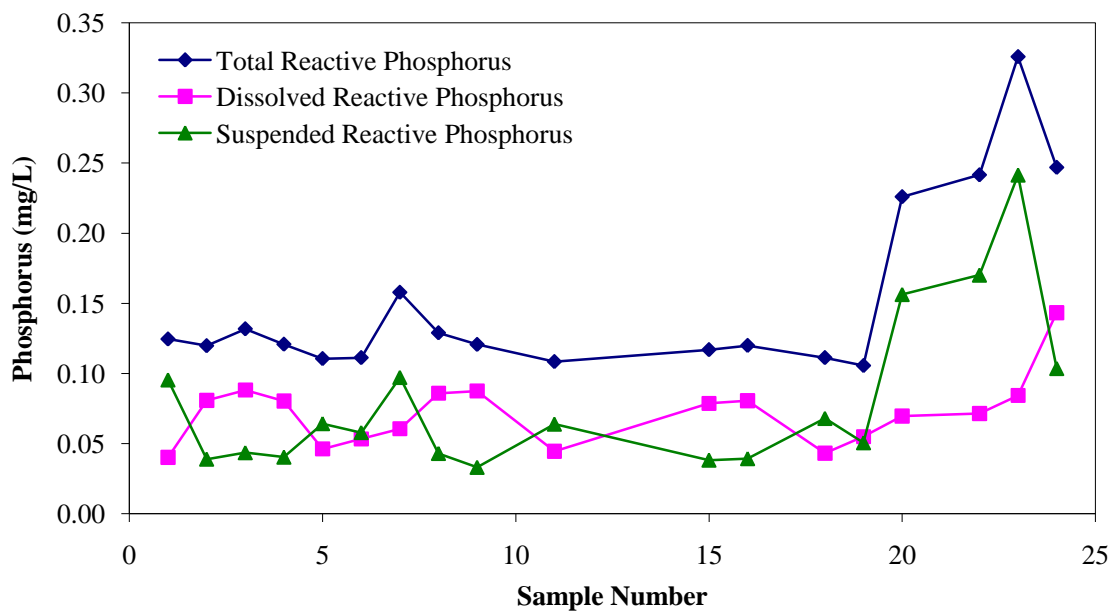


Figure 3.25 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of hourly samples collected at the Coralville site using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

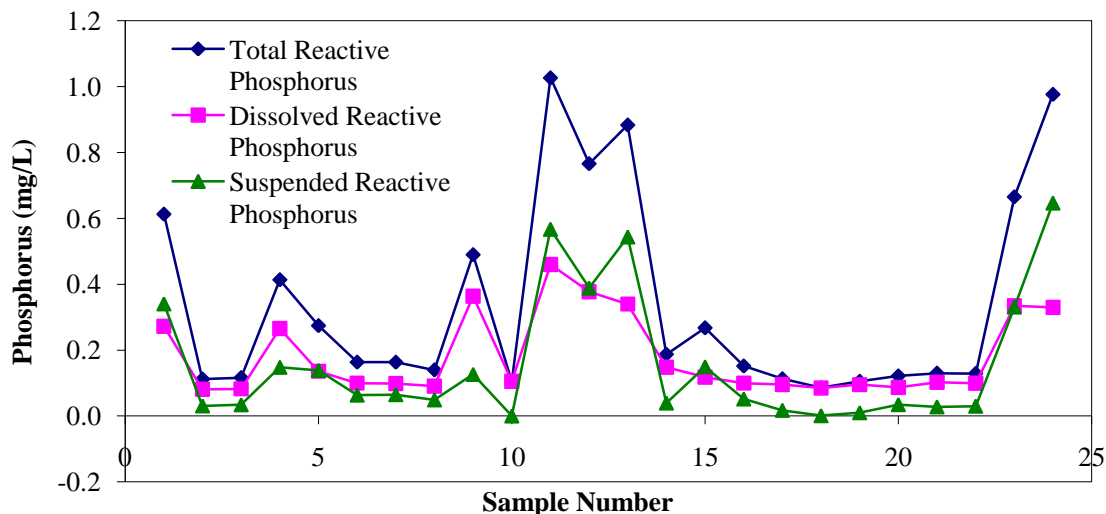


Figure 3.26 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of hourly samples collected at the Amana site using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24 graphed on the same scale as Figures 3.25 and 3.26 for comparison.

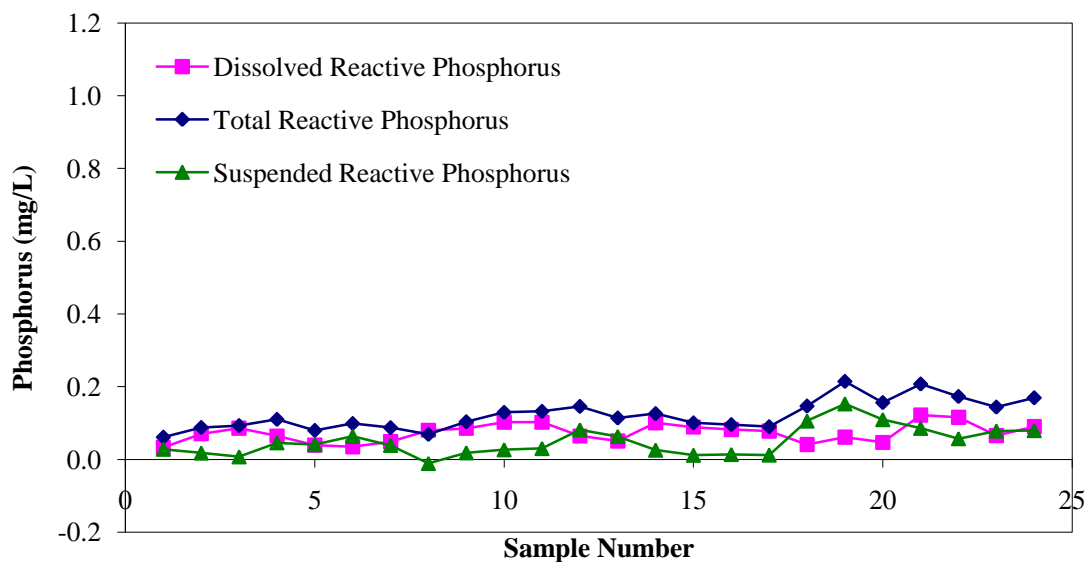


Figure 3.27 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of hourly samples collected at the Oxford site using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24 graphed on the same scale as Figures 3.24 and 3.26 for comparison.

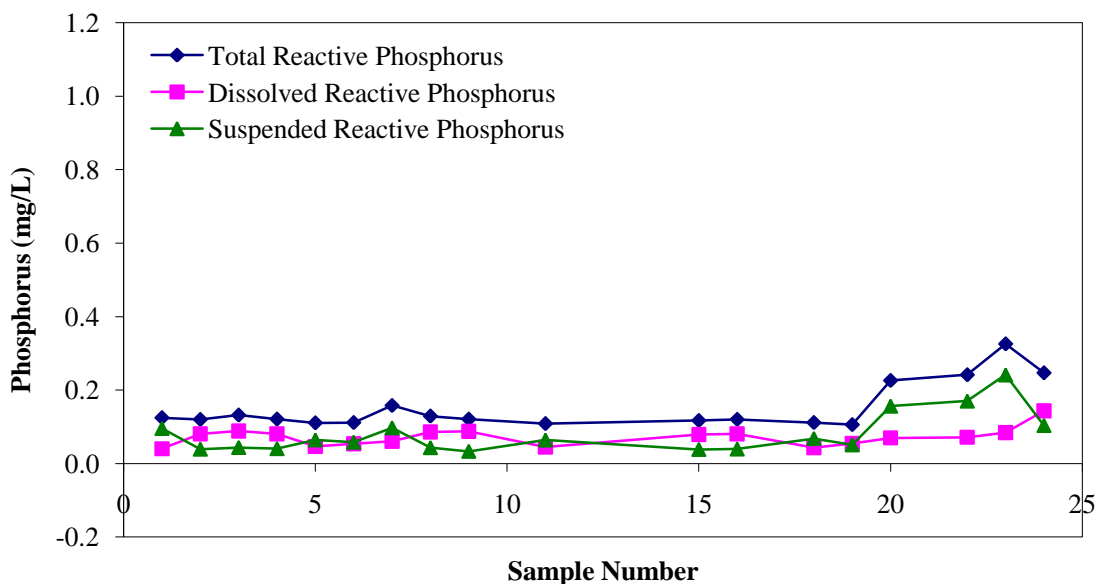


Figure 3.28 Total, dissolved, and suspended reactive phosphorus concentrations in mg/L of hourly samples collected at the Coralville site using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24 graphed on the same scale as Figures 3.24 and 3.25 for comparison.

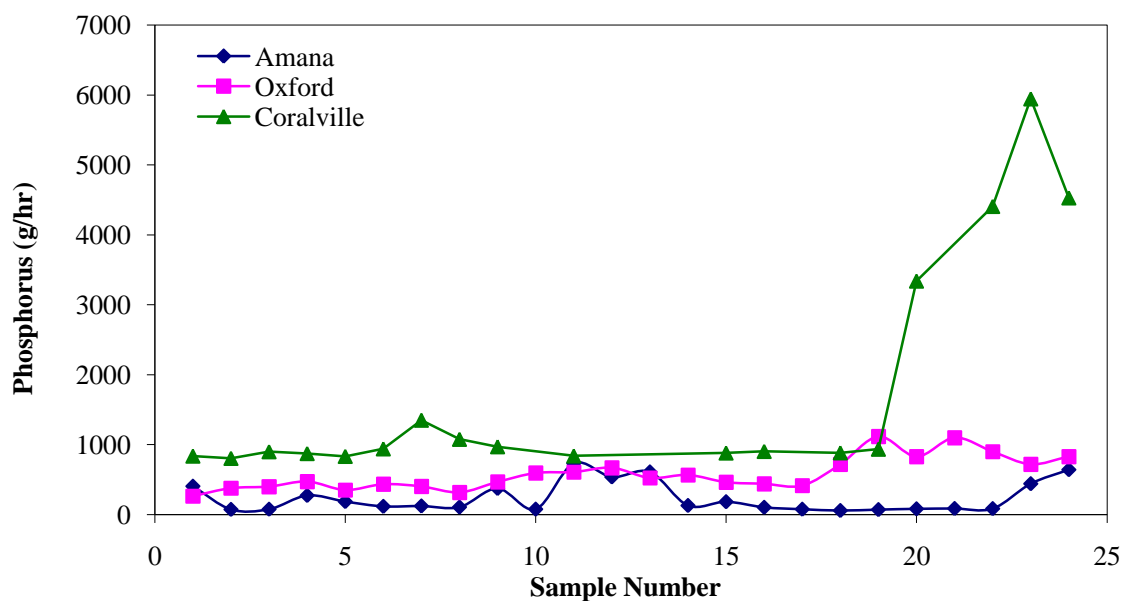


Figure 3.29 Total reactive phosphorus loadings in g/hr of hourly samples collected at Amana, Oxford, and Coralville using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

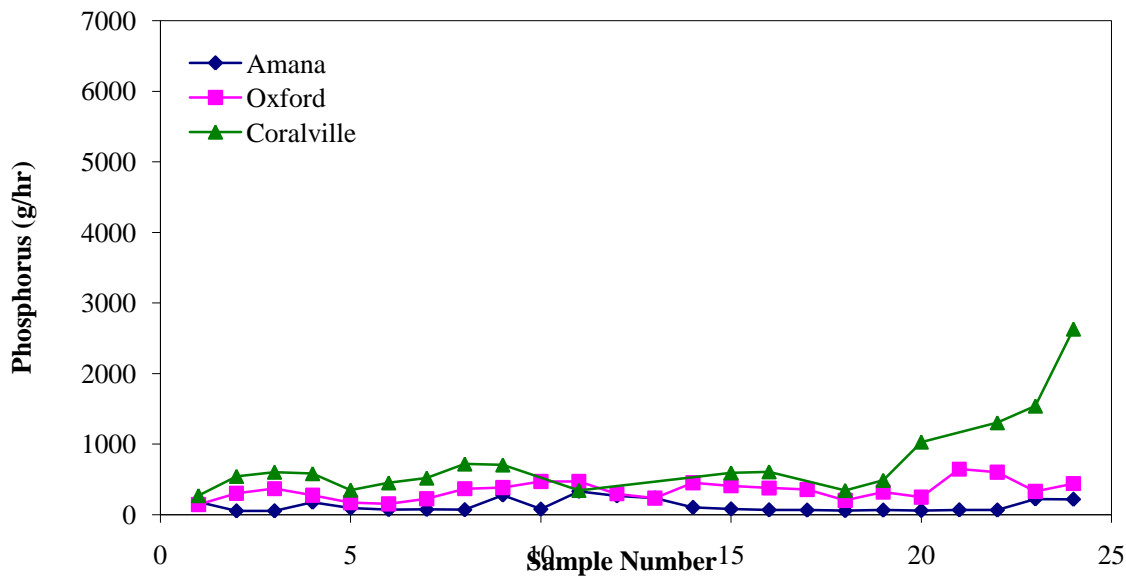


Figure 3.30 Dissolved reactive phosphorus loadings in g/hr of hourly samples collected at Amana, Oxford, and Coralville using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

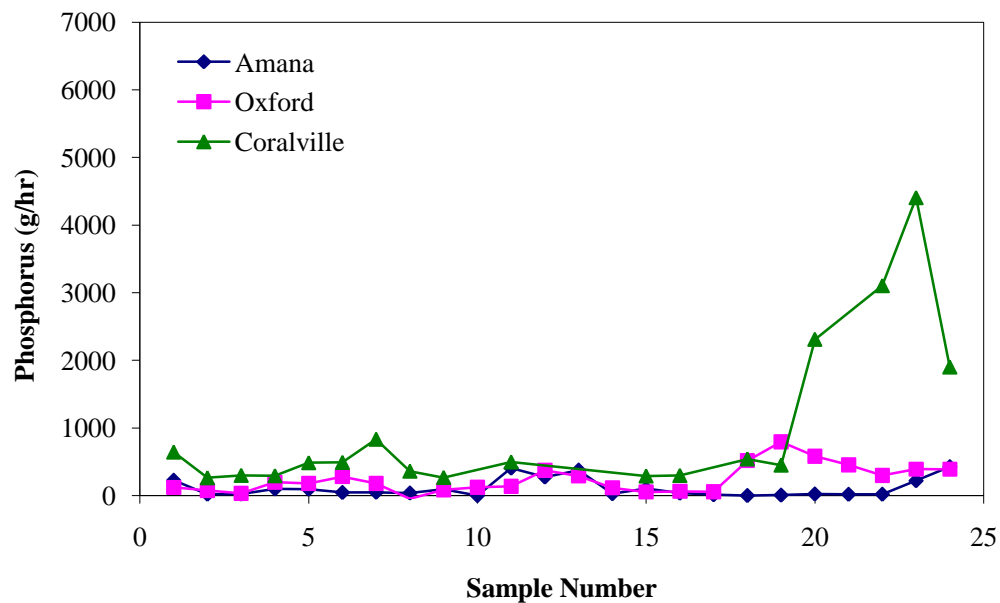


Figure 3.31 Suspended reactive phosphorus loadings in g/hr of hourly samples collected at Amana, Oxford, and Coralville using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

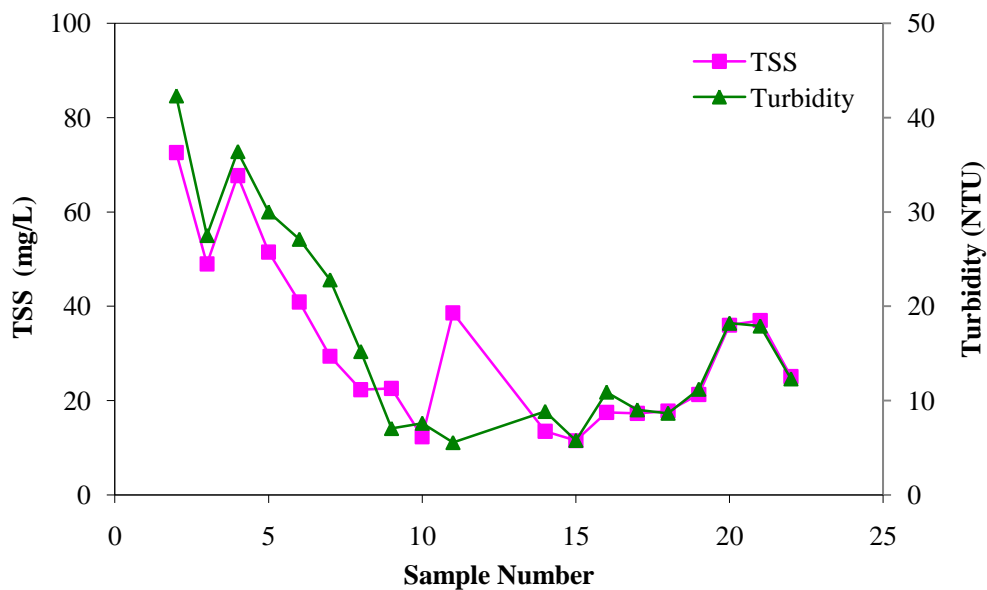


Figure 3.32 Turbidity (NTU) and TSS (mg/L) of hourly samples collected at Amana using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24. Samples 11, 12, 13, 23, and 24 were discarded due to sampling errors.

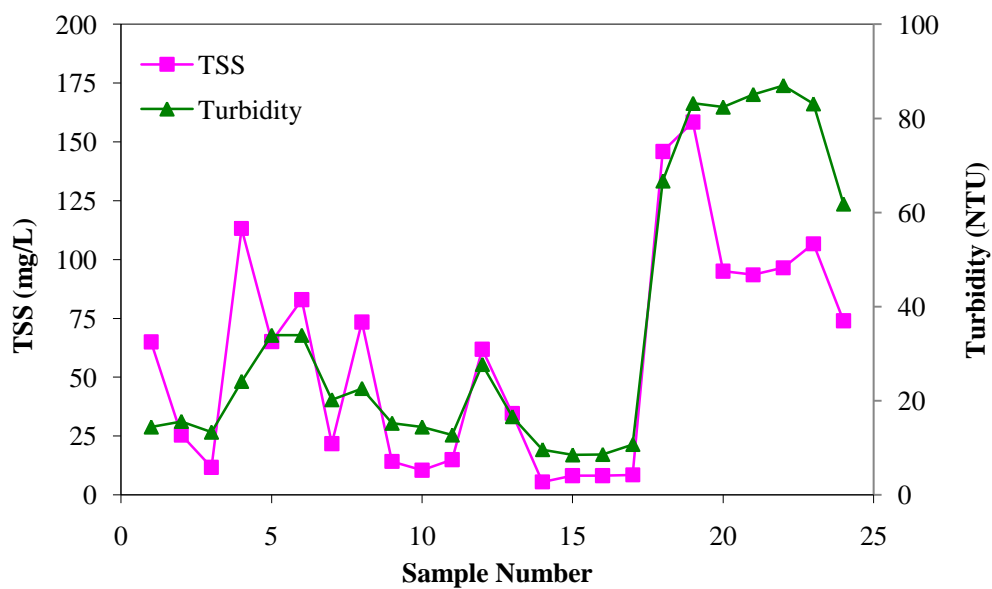


Figure 3.33 Turbidity (NTU) and TSS (mg/L) of hourly samples collected at Oxford using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

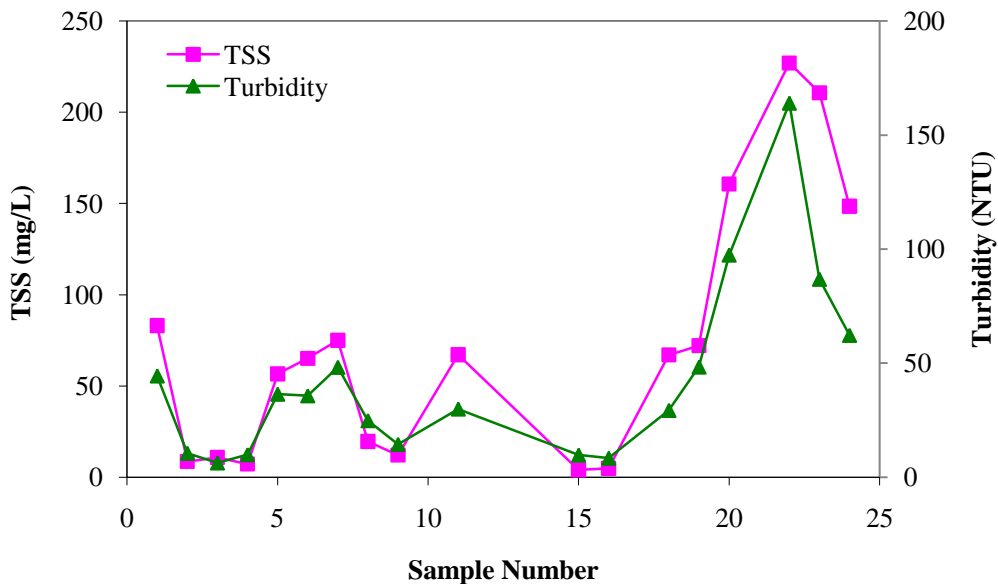


Figure 3.34 Turbidity (NTU) and TSS (mg/L) of hourly samples collected at Coralville using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

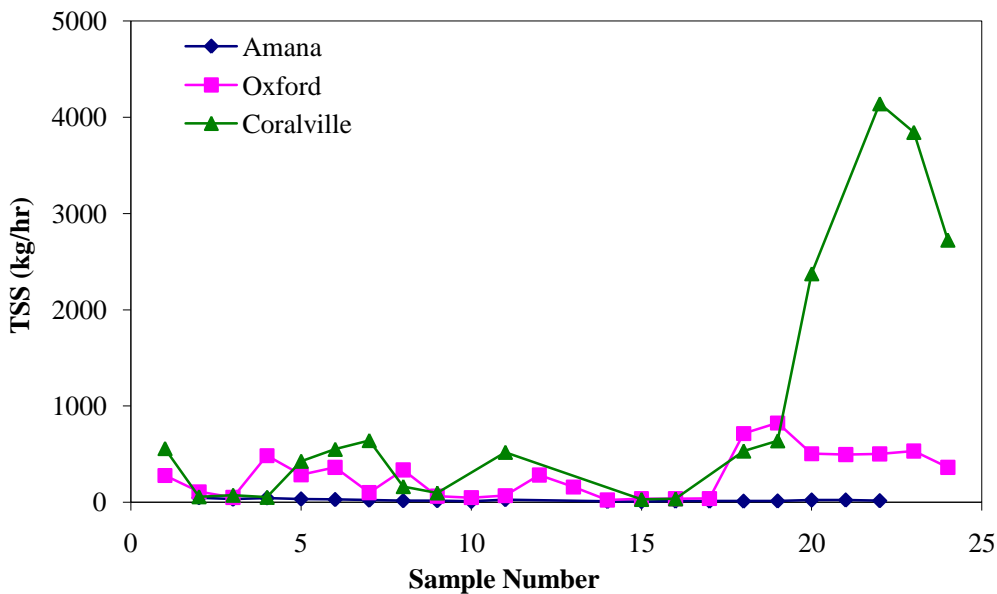


Figure 3.35 TSS loadings in kg/hr of hourly samples collected at Amana, Oxford, and Coralville using an automatic Isco sampler from 3:00 am on October 23 until 2:00 am on October 24.

CHAPTER 4

CONCLUSIONS

The purpose of this research was to quantify reactive phosphorus in Clear Creek and to understand how it changes with space and time. The objectives with corresponding conclusions are shown below:

1. Determine if most of the mass of reactive phosphorus is traveling during base flow or high flow events.

Most of the mass of reactive phosphorus in Clear Creek is traveling during the flow events. Five of the twenty-eight grab samples were collected during high flow and these samples contributed 94%, 91%, and 90% of the mass of total reactive phosphorus for the entire season at the Amana, Oxford, and Coralville sites, respectively.

2. Determine whether the majority of reactive phosphorus in Clear Creek is dissolved or attached to solids.

A majority of the mass of reactive phosphorus transported in Clear Creek is associated with solids. About two-thirds of the total reactive phosphorus in Clear Creek was suspended while the remaining one-third was dissolved.

3. Determine the sources of reactive phosphorus and whether or not any “hotspots” exist.

The Amana site, which is nearest to the headwaters, was found to be the only phosphorus hotspot and a significant source of dissolved reactive phosphorus. During a storm event, much higher reactive phosphorus concentrations were measured at this site than at the other two sites indicating that land surrounding the headwaters is a significant source for phosphorus runoff.

Weekly grab samples were collected at three locations along Clear Creek throughout the six month sampling period. During this time, there were five instances when samples we collected during high flow. An analysis of the weekly grab samples revealed that more mass of reactive phosphorus moved during the five high flow events sampled than moved the rest of the season under the lower flow conditions. This was found to be especially true for the suspended reactive phosphorus mass flux where approximately 94% of the mass was transported during the five events. Approximately 90% of the mass of total reactive phosphorus was transported during the periods of high flow while 83% of the dissolved reactive phosphorus was moved at these events.

The weekly grab samples collected from three sites also showed that the majority of the reactive phosphorus in Clear Creek was attached to particles. Generally, under lower flow conditions, the greater part of the total reactive phosphorus was dissolved while less was suspended. During high flow events, however, the suspended reactive phosphorus dominated because there was a much larger mass of solids in the stream caused by runoff from the storm and reactive phosphorus was attached to these particles. Although dissolved reactive phosphorus concentrations were higher for most of the season, suspended reactive phosphorus dominated because, as previously mentioned, the majority of the mass of reactive phosphorus moved during the five high flow events.

No reactive phosphorus hotspots were evident from analysis of the weekly grab samples or twelve bridge samplings. Rather, there was a gradual increase in concentration and loading as one proceeds downstream. This indicates that there are sources of phosphorus all along Clear Creek. Since flows increase as location along Clear Creek approaches the confluence of the Iowa River, it must follow that significant a

significant mass of phosphorus is entering downstream as well. If this was not the case, concentrations would decrease as sampling location moved downstream due to dilution from the increased flow.

A phosphorus hotspot was revealed by the 24 hour sampling with the automatic Isco sampler which showed the Amana site was as a hotspot based on dissolved phosphorus concentrations. The analysis of samples collected during this period exposed that peak total reactive phosphorus concentrations at Amana were more than three times as large as the peak concentrations at either of the other two sites. Furthermore, the average total reactive phosphorus concentrations at Amana were approximately twice as high as Oxford and Coralville. That the automatic samplers captured a relatively small storm is an important factor in revealing Amana as a hotspot. This was not exposed in the high flow events from the weekly grab samples because the storms were so powerful that the enormous influx of solids caused suspended reactive phosphorus to dominate and over shadow Amana's contribution. The storm caught by the automatic samplers was small enough to reveal Amana as a significant source of phosphorus in runoff.

The weekly grab samples provided information about how reactive phosphorus concentration changed over time. No clear trends were evident in the relatively low flow reactive phosphorus concentrations throughout the sampling season. Most of the high flow events were occurred early in the sampling season which is intuitive since it is well know that the majority of storms and rainfall occur in the spring months. The sampling of several bridges provided insight on how the reactive phosphorus in Clear Creek changes with location. Analyses of these samples revealed that reactive phosphorus concentrations are lowest near the headwaters and increase as the sampling locations

approach the confluence of Clear Creek and the Iowa River. This conclusion was also support by the weekly grab samples which commonly displayed the highest reactive phosphorus concentrations closest at Coralville and the lowest concentrations at Amana.

The weekly grab samples and bridge samplings provided a great deal of information on the reactive phosphorus dynamics in Clear Creek from June to December. In the future, it would be beneficial to begin sampling earlier in the year in order to capture more of the early spring storms as well as the effects of planting and fertilizing row crops in the spring. Much more hourly data during storms is also needed for a comprehensive understanding of the phosphorus transport. The small storm sampled for this research revealed Amana as an intense source of reactive phosphorus which was not evident from the grab samples. It is possible that other sources are currently being overlooked as well but could be made apparent from more storm sampling. In the future it would be advantageous to sample storms throughout the season; beginning in early spring and ending in late fall. It would also be useful to sample hourly during larger storm events and at to begin sampling later in the storm in order to catch the effects of the rainfall on all sites.

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APPENDIX A

MEASURED ATTRIBUTES OF WEEKLY GRAB SAMPLES

Table A.1 Measured attributes of weekly grab samples from the Amana site from June 4, 2010 to December 6, 2010.

Date	Turbidity (NTU)	Temperature (°F)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
06/04	16.7	66.0	-	0.093	0.046	0.047
06/09	14.5	69.5	-	0.120	0.072	0.048
06/16	47.1	62.0	106	0.252	0.098	0.154
06/22	152	66.0	242	0.557	0.222	0.335
06/28	24.0	65.0	52	0.161	0.084	0.077
07/06	42.9	65.0	103	0.166	0.125	0.041
07/12	8.68	65.0	15.9	0.109	0.055	0.054
07/20	17.3	67.0	51.6	0.105	0.077	0.028
07/26	15.6	68.0	29.8	0.095	0.082	0.013
08/02	14.9	67.0	25.2	0.121	0.102	0.019
08/08	8.98	78.0	12.8	0.114	0.100	0.014
08/18	6.63	72.0	14.1	0.115	0.095	0.020
08/24	14.3	67.0	27.1	0.111	0.088	0.023
08/30	14.1	71.0	25.7	0.108	0.078	0.030
09/07	8.94	72.0	10.8	0.101	0.100	0.001
09/14	17.3	79.0	26.2	0.089	0.106	-0.017
09/21	10.1	68.5	14.0	0.109	-	-
09/24	114	67.5	213	0.538	0.324	0.214
10/03	7.00	60.0	18.3	0.092	0.069	0.023
10/14	6.79	55.0	16.9	0.089	0.065	0.024
10/19	9.78	53.5	15.9	0.107	0.067	0.040
10/26	9.23	54.0	9.5	0.102	0.063	0.039
11/01	6.44	50.0	9.6	0.099	0.061	0.038
11/09	5.38	55.5	7.2	0.101	0.075	0.026
11/17	7.90	45.0	9.8	0.066	0.048	0.018
11/22	5.30	49.0	4.3	0.064	0.059	0.005
11/29	13.5	44.0	19.0	0.053	0.032	0.021
12/06	15.0	33.0	28.0	0.031	0.014	0.017

Table A.1 Measured attributes of weekly grab samples from the Oxford site from June 4, 2010 to December 6, 2010.

Date	Turbidity (NTU)	Temperature (°F)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
06/04	43.0	68.0	-	0.216	0.090	0.126
06/09	22.0	71.0	40.0	0.175	0.095	0.080
06/16	150	66.0	310	0.495	0.136	0.359
06/22	98.0	67.0	197	0.431	0.145	0.286
06/28	66.9	65.5	150	0.297	0.111	0.186
07/06	540	71.0	670	0.518	0.215	0.303
07/12	32.5	67.5	62.1	0.138	0.066	0.072
07/20	23.1	69.0	40.9	0.15	0.092	0.058
07/26	23.9	73.5	35.3	0.153	0.095	0.058
08/02	31.1	71.0	52.0	0.178	0.142	0.036
08/08	20.3	75.0	36.3	0.165	0.134	0.031
08/18	28.8	71.0	54.4	0.187	0.127	0.060
08/24	26.6	70.0	44.2	0.171	0.103	0.068
08/30	14.6	74.0	21.0	0.153	0.107	0.046
09/07	77.1	66.5	101	0.213	0.134	0.079
09/14	14.2	79.0	18.4	0.128	0.117	0.011
09/21	23.4	70.5	34.4	0.168	-	-
09/24	1070	66.5	1098	0.936	0.384	0.552
10/03	22.6	57.0	35.7	0.133	0.074	0.059
10/14	9.40	54.0	11.0	0.107	0.067	0.040
10/19	7.25	51.0	6.9	0.108	0.060	0.048
10/26	11.6	56.0	12.4	0.152	0.100	0.052
11/01	8.22	48.0	15.2	0.119	0.061	0.058
11/09	5.07	52.0	4.3	0.113	0.080	0.033
11/17	5.85	42.0	7.0	0.084	0.046	0.038
11/22	6.59	47.5	4.5	0.068	0.040	0.028
11/29	25.3	40.5	53.0	0.122	0.032	0.090
12/06	21.9	32.0	4.8	0.067	0.010	0.057

Table A.3 Measured attributes of weekly grab samples from the Coralville site from June 4, 2010 to December 6, 2010.

Date	Turbidity (NTU)	Temperature (°F)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
06/04	55.7	73.0	-	0.270	0.090	0.180
06/09	39.4	74.0	-	0.220	0.104	0.116
06/16	380	67.0	591	0.695	0.154	0.541
06/22	128	70.0	239	0.509	0.108	0.401
06/28	108	69.0	223	0.471	0.126	0.345
07/06	770	70.0	895	0.549	0.157	0.392
07/12	41.4	70.0	79.8	0.166	0.142	0.024
07/20	25.8	71.0	50.1	0.139	0.120	0.019
07/26	26.6	74.0	44.6	0.179	0.120	0.059
08/02	28.3	73.0	47.0	0.196	0.162	0.034
08/08	26.2	76.0	43.3	0.219	0.142	0.077
08/18	58.2	72.0	100	0.237	0.134	0.103
08/24	45.7	72.0	64.3	0.221	0.130	0.091
08/30	15.3	74.0	24.0	0.174	0.125	0.049
09/07	27.2	69.0	52.9	0.202	0.125	0.077
09/14	12.9	81.0	18.7	0.154	0.132	0.022
09/21	25.5	72.0	42.9	0.203	-	-
09/24	1301	67.5	1303	0.968	0.175	0.793
10/03	18.0	56.0	30.3	0.161	0.092	0.069
10/14	14.0	57.5	12.2	0.126	0.054	0.072
10/19	9.71	52.5	10.0	0.123	0.066	0.057
10/26	30.5	56.5	43.7	0.190	0.127	0.063
11/01	8.55	49.0	6.2	0.130	0.045	0.085
11/09	4.17	54.0	3.6	0.087	0.042	0.045
11/17	6.54	43.0	4.8	0.095	0.049	0.046
11/22	7.15	48.0	5.1	0.077	0.052	0.024
11/29	69.1	42.0	122	0.267	0.027	0.240
12/06	45.8	33.0	5.7	0.101	0.006	0.095

APPENDIX B

MEASURED ATTRIBUTES OF SEVERAL BRIDGE SAMPLING

Table B.1 Measured attributes of eight bridge sampling conducted May 27, 2010.

Miles from Iowa River	Turbidity (NTU)	Temperature (°F)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
25.39	-	-	-	0.162	0.077	0.085
20.17	-	-	-	0.211	0.100	0.112
16.26	-	-	-	0.264	0.115	0.149
13.62	-	-	-	0.448	0.113	0.336
9.73	-	-	-	0.564	0.109	0.455
6.89	-	-	-	0.508	0.174	0.334
2.8	-	-	-	0.495	0.127	0.368
0.43	-	-	-	0.561	0.147	0.414

Table B.2 Measured attributes of twelve bridge sampling conducted July 12, 2010.

Miles from Iowa River	Turbidity (NTU)	Temperature (°F)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
25.39	8.68	65.0	15.9	0.109	0.055	0.054
20.17	22.6	66.0	44.7	0.091	0.073	0.018
18.06	24.5	66.0	48.3	0.119	0.070	0.049
16.26	28.8	66.5	54.3	0.131	0.067	0.064
13.62	32.5	67.5	62.1	0.138	0.066	0.072
10.39	36.9	68.0	75.9	0.150	0.082	0.068
9.73	38.2	69.0	76.1	0.174	0.083	0.091
8.43	36.7	69.0	69.7	0.169	0.107	0.062
6.89	37.9	69.0	72.8	0.164	0.117	0.047
4.85	39.4	70.0	77.3	0.187	0.147	0.040
2.8	41.4	70.0	79.8	0.166	0.142	0.024
0.43	17.7	70.0	25.2	0.175	0.155	0.020

Table B.3 Measured attributes of twelve bridge sampling conducted September 21, 2010.

Miles from Iowa River	Turbidity (NTU)	Temperature (°F)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
25.39	10.1	68.5	-	0.109	-	-
20.17	30.5	69.0	-	0.141	0.085	0.056
18.06	27.0	69.5	-	0.139	0.086	0.053
16.26	25.1	70.0	-	0.158	0.090	0.068
13.62	23.4	70.5	-	0.168	-	-
10.39	23.9	71.0	-	0.176	0.113	0.063
9.73	24.5	71.5	-	0.179	0.107	0.072
8.43	21.0	70.5	-	0.176	0.115	0.060
6.89	19.3	71.0	-	0.182	0.100	0.081
4.85	20.1	71.0	-	0.196	0.116	0.080
2.80	25.5	72.0	-	0.203	-	-
0.43	26.7	72.0	-	0.213	0.132	0.081

APPENDIX C

MEASURED ATTRIBUTES OF HOURLY SAMPLES DURING STORM EVENT

Table C.1 Measured attributes of hourly samples collected at the Amana site using an automatic Isco sampler beginning with sample number 1 at 3:00 am on October 23 and commencing with sampler number 24 at 2:00 am on October 24.

Sample Number	Turbidity (NTU)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
1	3700	6802	0.613	0.272	0.341
2	42.3	72.6	0.112	0.081	0.031
3	27.5	49.0	0.116	0.082	0.034
4	36.4	67.7	0.414	0.266	0.148
5	30.0	51.5	0.274	0.136	0.138
6	27.1	40.9	0.163	0.100	0.063
7	22.8	29.4	0.163	0.099	0.065
8	15.2	22.3	0.140	0.091	0.049
9	7.04	22.6	0.490	0.364	0.126
10	7.60	12.3	0.105	0.105	0.000
11	5.55	38.6	1.027	0.460	0.567
12	2550	4442	0.766	0.378	0.389
13	1531	1741	0.884	0.340	0.544
14	8.85	13.5	0.187	0.148	0.039
15	5.78	11.5	0.268	0.118	0.149
16	10.9	17.5	0.152	0.100	0.052
17	9.02	17.3	0.113	0.096	0.017
18	8.66	17.8	0.086	0.085	0.001
19	11.2	21.3	0.105	0.095	0.010
20	18.2	36.0	0.122	0.087	0.035
21	17.9	37.0	0.130	0.102	0.028
22	12.3	25.1	0.129	0.099	0.030
23	1638	2932	0.665	0.334	0.331
24	539	1378	0.977	0.330	0.647

Table C.2 Measured attributes of hourly samples collected at the Oxford site using an automatic Isco sampler beginning with sample number 1 at 3:00 am on October 23 and commencing with sampler number 24 at 2:00 am on October 24.

Sample Number	Turbidity (NTU)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
1	14.4	65	0.062	0.033	0.028
2	15.6	25.4	0.088	0.070	0.018
3	13.3	11.7	0.093	0.086	0.007
4	24.1	113.2	0.110	0.064	0.046
5	33.9	65.1	0.080	0.039	0.041
6	33.9	83	0.099	0.035	0.064
7	20.2	21.8	0.088	0.049	0.039
8	22.6	73.4	0.069	0.080	-0.011
9	15.2	14.2	0.104	0.085	0.018
10	14.4	10.5	0.130	0.103	0.027
11	12.7	15	0.132	0.102	0.030
12	27.7	61.9	0.146	0.064	0.081
13	16.6	34.6	0.114	0.051	0.063
14	9.6	5.5	0.126	0.100	0.026
15	8.47	8.2	0.101	0.089	0.012
16	8.57	8.2	0.096	0.082	0.014
17	10.7	8.5	0.090	0.078	0.012
18	66.7	145.9	0.147	0.041	0.106
19	83.2	158.4	0.214	0.062	0.153
20	82.4	95.1	0.156	0.047	0.110
21	85.1	93.5	0.207	0.122	0.086
22	87	96.5	0.173	0.116	0.057
23	83.1	106.7	0.144	0.066	0.078
24	61.8	74	0.170	0.090	0.080

Table C.3 Measured attributes of hourly samples collected at the Coralville site using an automatic Isco sampler beginning with sample number 1 at 3:00 am on October 23 and commencing with sampler number 24 at 2:00 am on October 24.

Sample Number	Turbidity (NTU)	Total Suspended Solids (mg/L)	Total Reactive Phosphorus (mg-P/L)	Dissolved Reactive Phosphorus (mg-P/L)	Suspended Reactive Phosphorus (mg-P/L)
1	44.4	83.1	0.125	0.040	0.095
2	10.5	8.6	0.120	0.081	0.039
3	6.26	10.8	0.132	0.088	0.044
4	9.88	7.2	0.121	0.080	0.040
5	36.4	56.6	0.111	0.046	0.064
6	35.7	65.1	0.111	0.053	0.058
7	48.2	75	0.158	0.061	0.097
8	24.8	19.6	0.129	0.086	0.043
9	14.4	12.1	0.121	0.088	0.033
10	-	-	-	-	-
11	29.9	67.1	0.108	0.045	0.064
12	-	-	-	-	-
13	-	-	-	-	-
14	-	-	-	-	-
15	9.7	4	0.117	0.079	0.038
16	8.33	4.8	0.120	0.081	0.039
17	-	-	-	-	-
18	29.3	67	0.111	0.043	0.068
19	48.3	72.1	0.106	0.055	0.051
20	97.4	160.7	0.226	0.070	0.156
21	-	-	-	-	-
22	164	227	0.242	0.071	0.170
23	86.8	210.7	0.326	0.084	0.242
24	62.2	148.5	0.247	0.143	0.104