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Understanding the critical role of a wetland in maintaining the ecosystem: A case study

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UNDERSTANDING THE CRITICAL ROLE OF A WETLAND IN MAINTAINING THE ECOSYSTEM: A CASE STUDY

An Abstract of a Thesis

Submitted

in Partial Fulfillment

of the Requirements for the Degree

Master of Science

Sushil Tuladhar

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ABSTRACT

Beaver Valley Wetland in north-east Iowa was studied to determine its functionality in filtering incoming contaminants from the surrounding agricultural fields. The study was conducted from May through November of 2011. Altogether 78 water samples (from 13 sites), 84 soil samples (from 14 sites), and some sediment samples were collected for chemical analysis. Heavy metals in three different soil categories, such as surface, 6" deep, and sediments were found to be at or below the acceptable concentrations, indicating no immediate concern for metal toxicity in the wetland environment. The chemical tracers that were used to study the sub-surface flow regime could not confirm the hypothesized flow regime in the shallow sub-surface. The possible scenarios are as follows; (1) the tracers may have entered the sand lenses and became immobilized, (2) the tracers may have moved in a curved flow path deeper than the injection holes, and (3) the tracers may have been lost to deep infiltration.

The analysis of water samples for various physical, chemical, and biological parameters focused on both spatial and temporal changes in water quality. The changes were significant during mid-summer compared to early and late summer. The probable causes for this could be the rainfall, algae growth and high organic load that were observed during the mid-summer. Most contaminants that were flushed from the surrounding areas into the wetland showed significant decrease in their concentrations going from the inlet to the outlet. High turbidity, high loads of TSS, and low DO were commonly observed at the inlet sites. The primary reason for the poor water quality condition at these sites was high organic loads and erodible agricultural soils in the

surrounding areas. The wetland shows a much better quality of water at the outlet sites, indicating that the unit has been functioning well in filtering various contaminants. Considerably high DO levels (21.3 mg/L at site W7), low turbidity (2.5 NTU at site W9), and low TSS (1.5 mg/L at site W8) values clearly prove this observation. The wetland being in proximity to the agricultural fields, some of the chemical parameters like nitrate, phosphorus, and chloride are of major concern. Interestingly, none of the sites showed dissolved nitrate in the water and the chloride level was well below the levels of concern. Absence of nitrate in the water could mean that nitrogen was consumed by microorganisms to extract oxygen and decompose the organic matter. On the other hand, the wetland is showing evidence of reducing phosphorus in the system by removing them from the water column. In Water Quality Index (WQI) analysis, the system varied from "medium" to "good" categories. Out of 75 water samples, 25 (33%) showed "medium" WQI values (50-70) and 50 samples (67%) were "good" (70-90).

From this short term study, it is concluded that the wetland has been performing well in filtering environmental contaminants. However, a long term water quality monitoring plan should be established to get a complete picture on the ecological functions of the wetland.

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This Study by: Sushil Tuladhar

Entitled: UNDERSTANDING THE CRITICAL OF A WETLAND IN MAINTAINING THE ECOSYSTEM: A CASE STUDY

has been approved as meeting the thesis requirement for the

Degree of Master of Science in Environmental Science.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Background

Wetlands are among the most important features in the environment that help maintain the quality of water by acting as a filter for various non-point source pollutants. The Environmental Protection Agency (EPA) defines wetlands as "transition zones where the flow of water, the cycling of nutrients, and the energy of the sun meet to produce a unique ecosystem characterized by hydrology, soils, and vegetation-making these areas very important features of a watershed" (USEPA, 2004).

Wetlands provide a link between terrestrial systems (such as upland forests and grasslands) and water bodies (such as lakes or rivers) as shown in Figure 1.

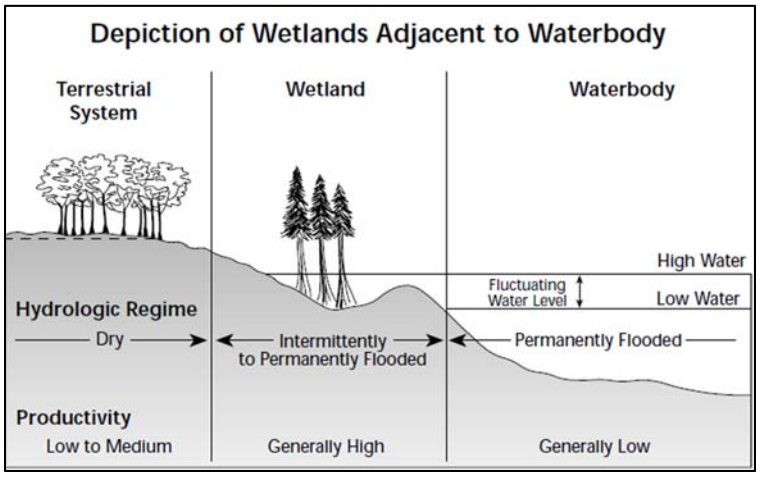


Figure 1: Wetland in between two ecosystems
(Source: USEPA, 2002)

They have important features that help in filtering various contaminants coming from the terrestrial environment, and in discharging the clean water to the lowland waterbody. Wetlands are often considered as “the kidneys of the landscape”. Wetlands, the areas of marshes, fens, or peat lands, can vary widely because of regional and local differences in soils, topography, climate, hydrology, water chemistry, vegetation, and other factors including human activities (USEPA, 2002). Wetlands can be classified based on hydrological features. In the United States, wetlands can be broadly categorized into marshes, swamps, bogs, and fens. Marshes are wetlands where soft-stemmed vegetation predominates (USEPA, 2004). These can be of two types: palustrine and lacustrine wetlands. Wetlands that are formed by glaciers are called palustrine wetlands, whereas lacustrine wetlands are open lake water and shallow edges of lakes. Such wetlands can be of different types which include tidal (coastal), non-tidal (inland), prairie potholes, freshwater, and saltwater. In such wetlands, water is generally fed either by surface water or groundwater. pH usually remains neutral with abundant nutrients (USEPA, 2012). Swamps, on the other hand, are wetlands that predominately have woody vegetation (USEPA, 2004). These occur either in freshwater or saltwater floodplains, and are generally fed by surface water (USEPA, 2001a). Bogs are freshwater wetlands that are formed in old glacial lakes and are characterized by spongy peat deposits, evergreen trees, and shrubs. Fens are freshwater wetlands which are characterized by grasses, sedges, reeds, and wildflowers (USEPA, 2004).

Wetlands are one of the important landscape features of the environment. They are not only the source of clean water but also provide many ecological functions and

values to both people and the environment. However, this important component of the environment has been recently threatened by human activities. The primary reason is converting available wetlands to farmland or urban land. In many cases, wetlands have been drained thereby reducing their water holding capacity. One of the factors that impacts most to the wetlands is agricultural practice. This practice has increased dramatically with the use of pesticides and fertilizers since the mid-1960s and the impact of such agrochemicals have added more nutrients and changed the water quality (Crumpton et al., 2006).

Urbanization is another factor that has made adverse impacts on the wetland. Direct impacts include habitat loss, suspended solids additions, hydrologic changes, and change in water quality. Similarly, indirect impacts include eutrophication, sedimentation, and loss of species (Azous & Horner, 1997). Due to human activities, many acres of wetlands have been lost and many others are under threats. Major loss in wetland acres was observed around the mid-1950s to mid-1970s. Although this loss has declined, it is estimated that about 60,000 acres are lost annually out of the remaining approximately 100 million wetland acres in the 48 contiguous states. Draining and development pressure are those key factors that cause the loss in wetland areas. Also, many created wetlands replace the diverse plant and animal communities with those which are in poor condition (USEPA, 2001b).

Therefore, the best way to know the conditions of the existing wetlands as well as their performance in the environment is through conducting water quality monitoring.

This will reveal the overall water chemistry of the wetland, and will identify the stressors that impose threat to them. Such monitoring would also help in the wetland restoration program to ensure better performance.

Values and Functions of Wetland

In the past, wetlands were considered as wastelands. There were large scale conversions of wetlands into farmland or agricultural or residential land ignoring their benefits and values. The importance of wetlands has been slowly recognized since the last couple of decades (Schwemm, 2005). Nowadays, wetlands are seen as one of the important components in the environment and many efforts have been going on to restore them. EPA along with the U.S. Army Corps of Engineers developed a number of programs for wetland restoration, conservation, and monitoring. Some of those include the partnership work with states, tribes, local governments, citizen organizations (like Association of State Wetland Managers, the National Association of Counties, local watershed associations, schools, and universities), incorporating them in EPA's watershed plans, developing national guidance or EPA's Five-Star Restoration Program monitoring, restoration, and protection of wetlands. EPA also works with various federal agencies like U.S. Fish and Wildlife Service, the U.S. Department of Agriculture, and the National Marine Fisheries Service to protect and restore wetlands (USEPA, 2001a).

The benefits of wetlands to the people are generally described in two terms: functions and values (Table 1). The various processes going within wetlands function with or without the presence of humans, but their value seems to be important because

such functions have proved to be useful to humans (Mitsch & Gosselink, 2000). Functions of wetlands include nutrient removal/transformation, sediment/toxicant retention, flood flow alteration, and groundwater discharge. On the other hand, values of wetlands include biodiversity, habitat, fishing, hunting, recreation, environmental quality values, and socioeconomic values (Tiner, 1984; Gerakis & Kalburtji, 1998).

Wetlands have an ability to transform and store nutrients and organic matter (Schwemm, 2005). They also act as a habitat and provide food to attract many wildlife species. Sometimes, they are used as a place by wildlife for their seasonal migration. Besides their high vegetative productivity, they are also important because of their filtering capacity. They help in filtering out pollutants that are likely to come from point (municipal and certain industrial wastewater effluents) and nonpoint sources (mine, agricultural, and urban runoff), by intercepting surface runoff, processing organic wastes, and reducing suspended sediments before they reach open water (Schwemm, 2005; USEPA, 2002). In addition to this, wetlands also help in regulating the stream flow and slowing down floodwaters.

Table 1: *List of major functions and values of wetlands*
(Source: Tiner, 1984)

Values:

Habitat

- Fish and Shellfish
- Waterfowl and other Birds
- Other Wildlife

Socio-Economic

- Flood Control
- Wave Damage Protection
- Erosion Control
- Groundwater Recharge and Water Supply
- Timber and Other Natural Products
- Energy Source
- Livestock Grazing
- Fishing and Shellfishing
- Hunting and Trapping
- Recreation
- Aesthetics
- Education and Scientific Research

Functions:

Environmental Quality

- Water Quality Maintenance
  - Pollution Filter
  - Sediment Removal
  - Oxygen Production
  - Nutrient Recycling
  - Chemical and Nutrient Absorption
- Aquatic Productivity
- Microclimate Regulator
- World Climate (Ozone Layer)

Hydrological Characteristics of Wetlands

The general classification of wetlands is based on their hydrological characteristics. It is the hydrological characteristics that make wetlands a unique ecosystem differing both from other aquatic and terrestrial ecosystems. Among many types of wetlands, those that are physically separated from surface water sources like lakes, rivers, and other water bodies can vary in water quality characteristics (Whigham & Jordan, 2003). Therefore, wetlands having lack of physical connection with streams or having weak interaction with groundwater are predominantly determined by four major hydrological processes: precipitation, runoff from snow melt, evapotranspiration, and infiltration. These wetlands are highly dependent on winter precipitation and snowmelt runoff (Waiser, 2006). The occurrence of such hydrological processes also help to transport energy, sediments, nutrients, and organic matter to, from and within wetlands (Pasi & Smardon, 2011). Figure 2 shows the effects of hydrology on wetland structure and function. Climate and geomorphology are the primary factors that govern the interaction of hydrology with other components of the ecosystem. Hydrology modifies and determines the physical environment, which in turn influences the biotic components of the ecosystem. In short, understanding hydrological characteristics is very important as they influence other ecological functions. This also determines the depth of water, flow patterns, and frequency of floods thereby influencing the soil biogeochemistry (Pasi & Smardon, 2011).

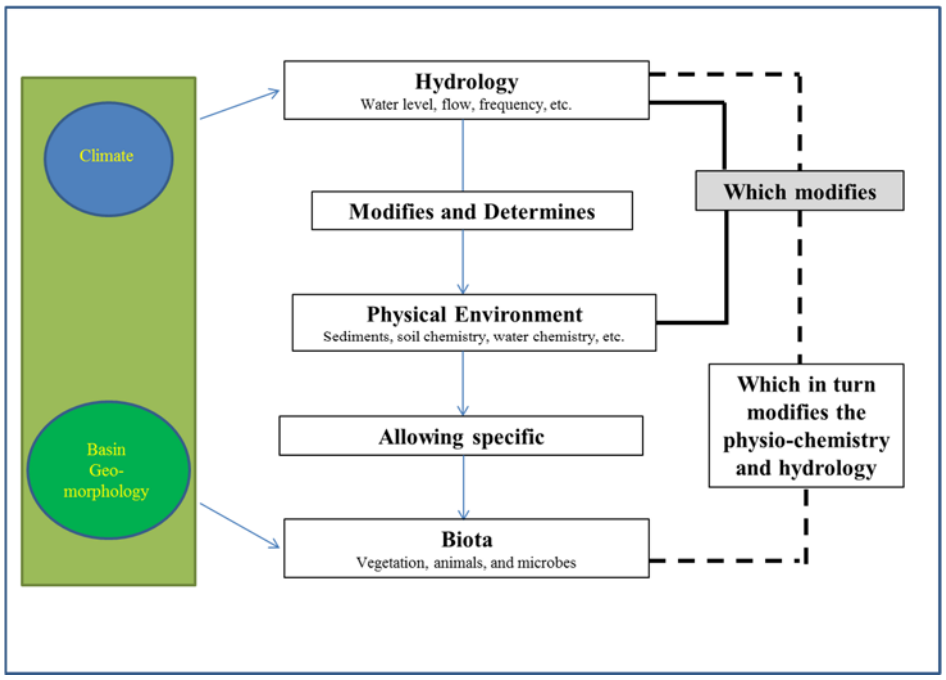


Figure 2: Effects of hydrology on wetland establishment and function (Source: Pasi & Smardon, 2011; Manomaipiboon, 2007)

Scenario of Wetlands in Iowa

Iowa was once a land rich in wetlands during the period of European settlement in the US. Most of these wetlands were found in north and central Iowa in the area called the Des Moines Lobe (Figure 3). This lobe was formed when glaciers covered Iowa 10,000-14,000 years ago. When the ice mass retreated, it left behind numerous depressions on the landscape filled with water. Those depressions with water were considered as wetlands (as small as less than an acre), and large lakes (IAN, 2001).

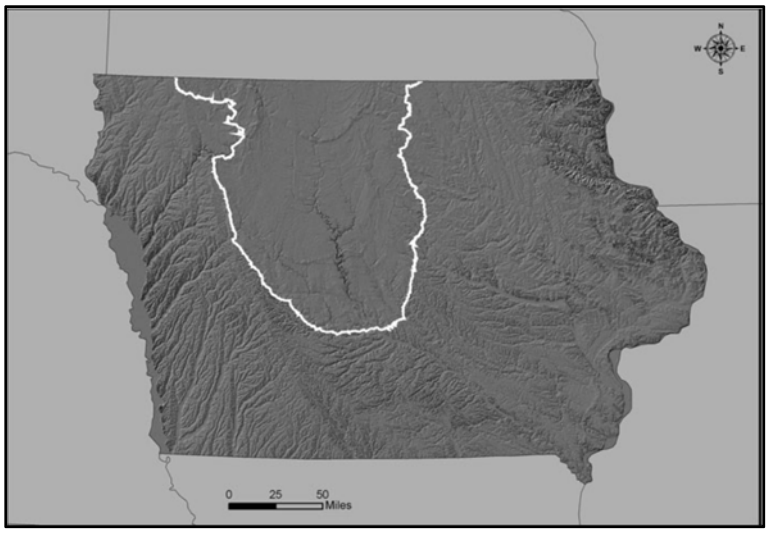


Figure 3: The Des Moines Lobe

It is estimated that there were about 1.4 million hectares of wetlands on the Des Moines Lobe in Iowa during the European settlement (Miller et al., 2012). In the past wetlands were highly recognized for their productivity and added impediments to development (Crumpton et al., 2012). Because of their high productivity, most of the wetlands were drained and converted to farmland. In Iowa alone, about 90% of wetlands have been drained for agriculture and development (NRCS, 2005). This also made farming possible in much of Iowa, Illinois, Indiana, and northwestern Ohio. On the other hand, wetlands were considered as unpleasant and unhealthy ecosystems by early settlers since wetlands were the habitat for flies and mosquitoes. They associated wetlands with diseases including malaria. Therefore, large scale drainage of wetlands began in the 1870s and 1880s for conversion to farmlands. The drainage had significantly reduced the total area of wetlands on the Des Moines Lobe, from about 3.5 million acres to 30,000 acres (nearly by 99%) by the mid-1970s (Crumpton et al., 2012). The importance of

wetlands was recognized later when many of them were drained for different purposes. Later, a variety of restoration programs were developed to restore these wetlands and their functions in the environment. By the early 1990s, thousands of wetlands had been restored in Iowa, including 94,000 to 143,000 acres of land in Des Moines Lobe. However, this increment in the last 40 years achieved only 3 to 4 percent of the wetlands that it had prior to European settlement (Crumpton et al., 2012).

Water Quality Improvement

Throughout the world, wetlands play an important role in the ecosystem because of their capability to improve water quality. Since they occupy the transition space between terrestrial and aquatic systems, they typically receive high surface runoff from the upland ecosystem. Factors like climate, landscape, and geomorphological processes can affect the quantity and quality of water entering the wetlands. When wetlands receive surface runoff, they store water, transform nutrients by chemical or biological actions, and retain sediments (Figure 4; Cook & Hauer, 2007). Therefore, wetlands are considered as a system of interacting biological and physical components that can change the fluxes coming from the surroundings (Moshiri, 1993). The purification processes in wetlands include settlement of suspended solids, diffusion of dissolved nutrients into the sediment, mineralization of organic materials, nutrient uptake by micro-organisms and vegetation, microbial transformations into gaseous components, and physiochemical adsorption and precipitation in the sediment (Verhoeven & Meuleman, 1999).

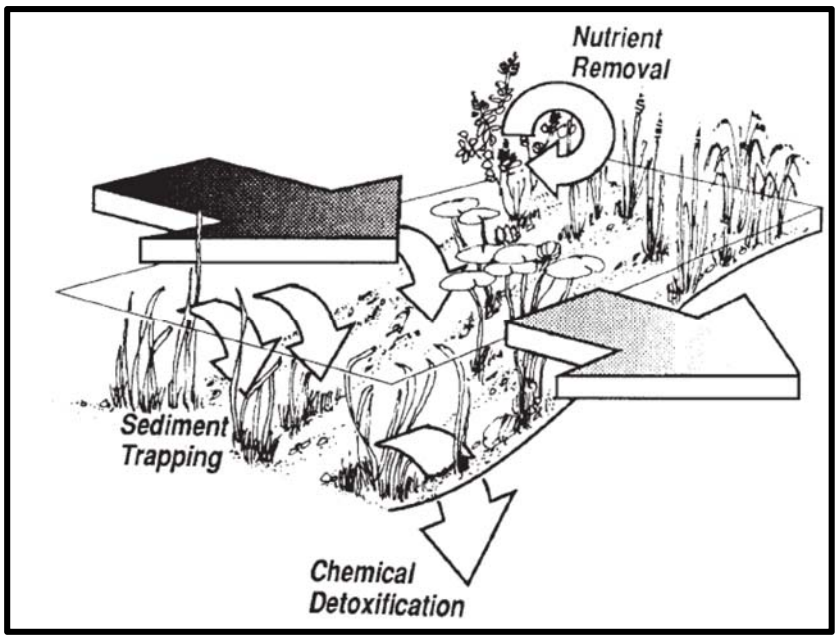


Figure 4: Processes involved in wetland purification
(Source: USEPA, 2002)

In general, wetlands having large volume of water allow enough contact with soil for extended periods of time (Barnes et al., 2002). When wetlands are adjacent to cultivated uplands, the chances of receiving sediments and nutrients after rainfall events are high. Excess sediments into the wetland through surface runoff might increase the turbidity that could reduce the photosynthetic process, oxygen concentration, impair respiration and may disturb the aquatic habitat. Therefore, when sediments enter the wetlands, the retention time allows them to settle out to the bottom, thereby benefiting the downstream water quality (Moshiri, 1993). Also, excessive nutrient flux might alter the filtering capacity of a wetland. Because of this, high inputs and outputs might determine whether a wetland could be a source or a sink for those nutrients. In addition, high transpiration to evaporation ratio may also concentrate the nutrients in wetland soils

(Barnes et al., 2002). However, the availability of limited water quality data makes it difficult to determine the nutrient criteria for wetland ecosystems (Beury et al., 2008). The major nutrients of concern in wetlands are nitrogen and phosphorus. These nutrients are likely to enter into the system from the agricultural fields due to surface runoff. When nutrients enter into the wetlands, they are either adsorbed or precipitated within the system. However, when wetland soils get fully saturated with excessive nutrients the capacity of wetland soils to retain nutrients declines. This eventually increases the total concentration of nutrients in the wetland water system. During the growing season, wetland vegetation can absorb large quantities of nutrients, but when these plants die much of them get released into the water. The removal of nutrients also depends on the size of the wetland because the smaller the size with high nutrient inputs, the lower would be the removal efficiency (Nichols, 1983).

Nitrogen

Nitrogen enters wetlands in both organic and inorganic forms. Organic nitrogen is usually present in dissolved and particulate fractions, whereas inorganic nitrogen is present in dissolved fractions (NH_4^+-N, NO_3^--N, and NO_2^--N). The organic forms can be removed through settling and burial, while inorganic forms undergo various biogeochemical reactions within the soil and water column (USEPA, 2008). The nitrogen, which enters into the wetland from various sources, is converted from one form to another by a variety of biochemical and chemical processes (Figure 5). The various

reactions like denitrification, adsorption, microbial action, mineralization, and nitrification effectively process nitrogen in the wetland.

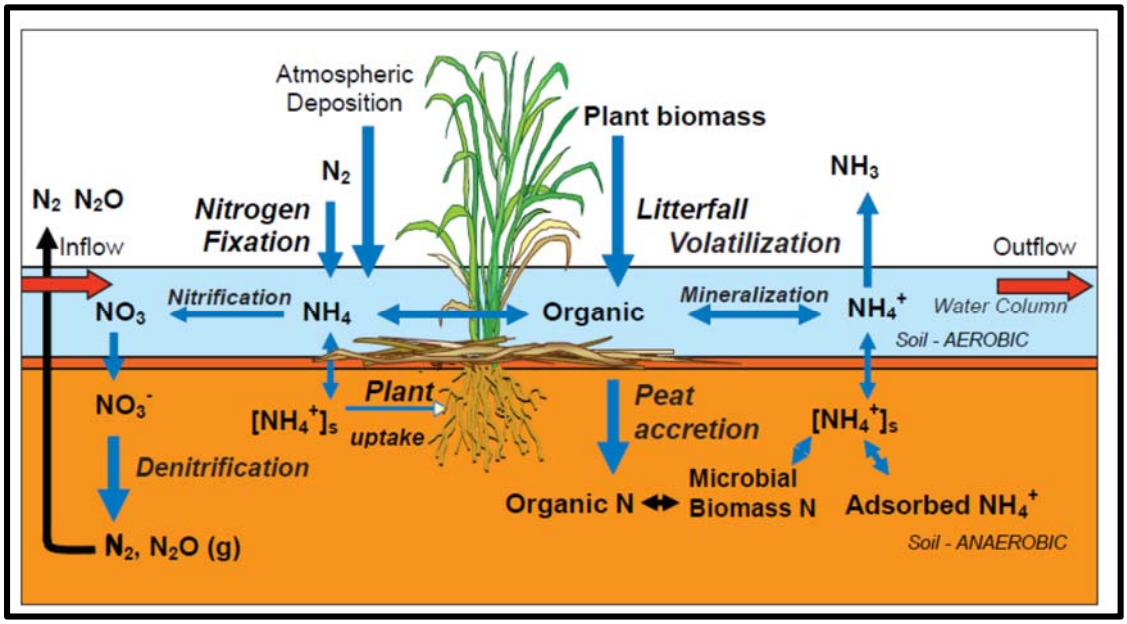


Figure 5: Schematic diagram of nitrogen cycles in wetlands
(Source: USEPA, 2008)

Denitrification is thought to be the primary mechanism for removing nitrogen that occurs in the anaerobic conditions of wetland ecosystems. In such conditions, anaerobic bacteria utilizes NO_3^- instead of free O_2 and converts NO_3^- to NO_2^- and then on to gaseous N_2O and N_2. Under acidic conditions (pH <6), this process occurs much more slowly than at neutral or alkaline pH. Such condition considers the biochemical reactions rather than chemical reactions to convert nitrogen to gaseous forms. This involves the microbial reduction of NO_3^- to NO_2^- followed by chemical conversion to gaseous

nitrogen (Nichols, 1983). Nitrification of NH_4^+ to NO_3^- takes place in aerobic conditions; the NO_3^- then diffuses slowly to anaerobic zone where it is denitrified.

Phosphorus

Phosphorus in different forms like dissolved inorganic phosphorus (DIP), organic phosphorus (DOP), particulate inorganic phosphorus (PIP), and particulate organic phosphorus (POP) enters into the wetland ecosystem from various sources, including surface runoff, agricultural wastewater, precipitation, and wastewater (Figure 6; USEPA, 2008).Water bodies with high levels of nutrients stimulate algae growth and as a result deplete the level of oxygen. This could be a potential threat to aquatic life and ecosystem health. The various combination of processes such as biotic (plant and microbial) uptake, sediment deposition, and chemical processes (including sorption by soil minerals, clay, and organic matter) may help in the retention of phosphorus in the wetland (Hogan & Walbridge, 2007). The retention process is determined by the performance of wetlands in different hydrologic conditions. In the dry season, wetlands act as an effective nutrient sink and favor retention for longer periods. However, in the wet period, inflow is usually high which makes the retention process shorter (Woltemade, 2000).

The phosphorus that enters into the wetland ecosystem could be altered in various forms due to both biotic (i.e., assimilation by vegetation, plankton, periphyton, and microorganisms) and abiotic (i.e., sedimentation, adsorption by soils, precipitation, and exchange processes between soil and the overlying water column) processes (USEPA, 2008). However, as phosphorus input continues over time, the concentrations are likely to

be higher in soils and plant tissues. In such case, soils can become saturated with phosphorus and desorb in the wetland water column (Hogan & Walbridge, 2007). Unlike other processes involved, wetland vegetation plays an important role in purifying contaminants. It supports the growth of decomposer microorganisms that help in breaking down dissolved organic materials. Since the nutrients get adsorbed onto the soil particles, these translocate from the soil to the plant shoot. The non-rooted plants such as algae and duckweed obtain nutrients from the water. Therefore, wetlands favor nutrient uptake more during the growing season (active vegetation growth) than in the non-growing season. Thus, the temporary storage of nutrients by the vegetation benefits downstream water quality (Nichols, 1983). In the wetland ecosystem, there are various processes that might release the phosphorus in the water column. Some of them include oxidation or decomposition of organic matter and desorption from clay and organic particles (Coon et al., 2000).

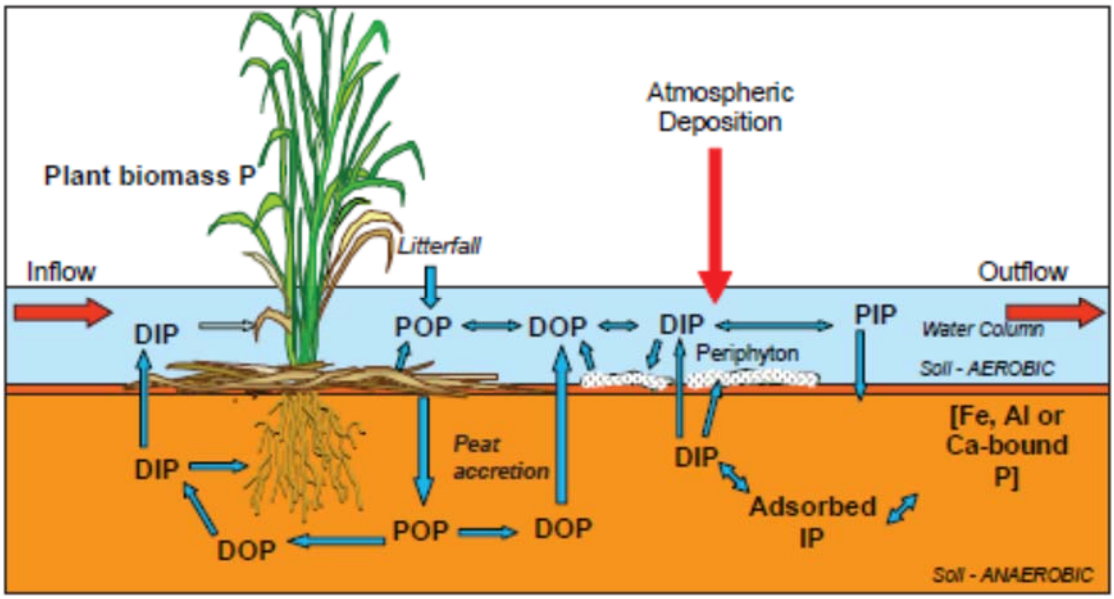


Figure 6: Schematic diagram of phosphorus cycles in wetlands
(Source: USEPA, 2008)

Importance of Monitoring Wetlands

Since wetlands are located between terrestrial and aquatic ecosystems, they intercept excess nutrients and sediments that are likely to come from the surrounding environment. They have the capacity to lower the concentration of many water contaminants including nitrogen, phosphorus, suspended solids, biochemical oxygen demand (BOD), trace metals, trace organics, and pathogens (Woltemade, 2000). However, such capacity is gradually pushed toward harmful conditions because of various anthropogenic activities such as agricultural practices, construction, hydrologic modification, urban runoff, and habitat modification. For example, excessive nutrients from agricultural fields or other sources may affect wetlands, causing too much vegetative growth and decay that can alter the water chemistry (USEPA, 2002). In

addition to this, the water chemistry of wetlands varies seasonally. For example, higher DO concentrations are observed from mid-November to mid-May than any other period of the year. This can be attributed to the existence of cold ambient temperature during this period. Similarly, wetlands in the period from May to November show higher conductivity and concentrated dissolved substances since the water level drops during this period (Horner et al., 1997). The retention time could be another factor that determines the performance of wetlands. For example, the retention time is shorter during the wet period (April through July). In such case, the removal capacity of the water contaminants becomes lower. On the other hand, during the drier period (August through November), the retention time becomes longer, thereby increasing the removal capacity of the contaminants (Woltemade, 2000). Therefore, along with different management practices, the monitoring of basic water quality parameters provides a better understanding on the performance of wetland ecosystems.

Water Quality Index

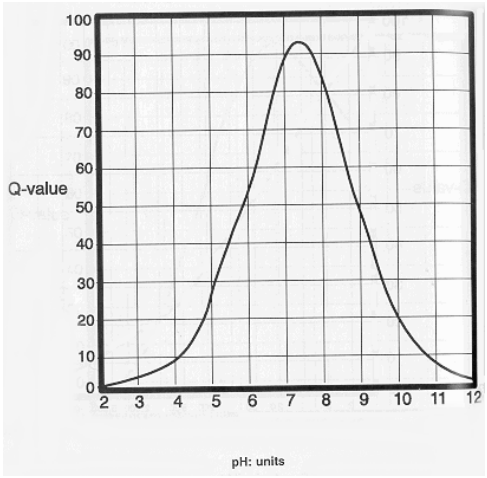
Water Quality Index (WQI) is a 100 point scale that summarizes and categorizes the quality of water bodies as excellent, good, medium, bad, and very bad. Several parameters can be considered to measure quality of certain water bodies at certain time and location. One of the standardized methods to measure the water quality for various surface water bodies is National Sanitation Foundation Water Quality Index (NSF-WQI) (Oram, 2013). It not only summarizes the overall water quality of water bodies but also presents the complex water quality information into simpler form that is understandable. It expresses overall water quality considering certain parameters, including pH,

temperature, dissolved oxygen, turbidity, fecal coliform, biochemical oxygen demand, total phosphates, nitrates, and total suspended solids. Table 2 gives the categorization of the water quality with a score ranging from 0-100.

Table 2: *NSF-WQI Score*
(Source: Oram, 2013)

Range	**Quality**
90-100	Excellent
70-90	Good
50-70	Medium
25-50	Bad
0-25	Very Bad

NSF-WQI is calculated based on Q-value and weighted factor of each water quality parameter. First of all, the field data are converted to a Q-value (also called Quality value). This can also be derived from the graph as shown in Figure 7. Then the Q-value is multiplied by weighted mean values (as given in Figure 7) to get the water quality index for that chemical. The results are then added to get the overall water quality index.



Factor	Weight
Dissolved oxygen	0.17
Fecal coliform	0.16
pH	0.11
Biochemical oxygen demand	0.11
Temperature change	0.10
Total phosphate	0.10
Nitrates	0.10
Turbidity	0.08
Total solids	0.07

Figure 7: Quality Index graph (Left) and Weighted Mean values (Right) (Source: Oram, 2013)

Heavy Metals in Wetland

Globally, heavy metal contamination in soils and water is one of the most serious environmental issues. This is due to their potential impact on human and environmental health. They are considered a nuisance to the environment because of their toxicity, persistence, and bioaccumulation problems (Aderinola et al., 2012). Naturally, heavy metals are persistent in the environment and are most likely to accumulate in sediments. They can come from geologic deposits or soil parent materials (Langner et al., 2011). The trace amounts of heavy metals such as Cr, Ni, Cu, Fe, and Zn in the aquatic system are essential to support biochemical roles in the life processes of aquatic plants and animals (Karpagavalli et al., 2012). However, their concentration can be increased by the action of anthropogenic activities which then become a major environmental concern. Some of these activities may include mining, manufacturing, and the use of synthetic products

such as pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge. Naturally, soils may contain heavy metals but rarely at toxic level (USDA & NRCS, 2000). Table 3 shows some of these activities, including disposal of industrial waste, acid mine drainage, fertilizers application, spillage of petrochemicals, wastewater irrigation, vehicle traffic, leaded gasoline, burning of fuel/oil, etc. (Wuana & Okieimen, 2011; Langner et al., 2011).

Table 3: *Different sources of heavy metals*
(Source: Langner et al., 2011; Luo et al., 2009)

Heavy metals	**Source**
Pb	Paints, leaded gasoline
Cd, Cr, Ni, Zn, Cu	Vehicle traffic, burning fuel and oil, metal production, waste incineration, vehicle brakes, road pavement tires, pressure-treated wood
As	Pressure-treated woods
Hg	Industrial activities

The generation of the metal wastes from the above sources could be carried away by runoff after precipitation and could deposit in the soil or surface water bodies and stay there for a long period of time. Since heavy metals can bioconcentrate and bioaccumulate in the food chain, these could have toxic effects on the aquatic as well as the terrestrial biotic life. These metals can also change the availability of other chemicals and nutrients in the aquatic ecosystem. Heavy metals, when released into the environment, cannot undergo microbial retention or chemical degradation. The most commonly found heavy metals in contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn),

cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). In 1993, Environmental Protection Agency (EPA) set the regulatory limits on heavy metals that are applied to soils (Table 4).

Table 4: *Regulatory limits on heavy metals*
(Source: USDA & NRCS, 2000)

Heavy metal	**Max. concentration in sludge (mg/kg or ppm)**	**Annual pollutant loading rates**		**Cumulative pollutant loading rates**	
		(kg/ha/yr)	**(lb/A/yr)**	**(kg/ha)**	**(lb/A)**
Arsenic	75	2	1.8	41	36.6
Cadmium	85	1.9	1.7	39	34.8
Chromium	3000	150	134	3000	2679
Copper	4300	75	67	1500	1340
Lead	420	21	14	420	375
Mercury	840	15	13.4	300	268
Molybdenum	57	0.85	0.80	17	15
Nickel	75	0.90	0.80	18	16
Selenium	100	5	4	100	89
Zinc	7500	140	125	2800	2500

Wetlands have the capacity to retain heavy metals both in water and sediments. Later, sediments release these heavy metals into the aquatic ecosystems and introduce toxicity. In comparison to water, sediments have high capacity to retain metals and could act as carriers and possible sources of pollution. Metals that are actually dissolved in the water are less than 0.1% whereas more than 99.9% of them are stored in sediments and soils (Alhashemi et al., 2011). Most importantly, wetlands help in removing metals from the water column. Depending on the specific metal and wetland characteristics, 20 to

100% of the metals could be removed (Vasilas & Vasilas, 2011; Sheoran & Sheoran, 2006). Wetlands are widely used as a sink for assimilating large amounts of environmental contaminants. The basic processes that are involved in purifying toxic contaminants include nutrient uptake by plants, degradation and oxidation of contaminants by bacteria, sedimentation and adsorption of particles, and dissolution of contaminants. Uptake of heavy metals by plants usually depends on both the metal and the soil conditions such as acidity and organic matter content (Sheoran & Sheoran, 2006; Nabulo et al., 2008). They remove metals from the water through biological uptake and surface adsorption. Therefore, the study of heavy metal distribution in sediments, which are generally expected to be higher than in the water column, would reduce the analytical errors and contamination problems that frequently arise during assessments of water bodies. The study of heavy metals in sediments is also important because many aquatic biota that feed on sediments might be exposed to these metals. Lastly, since wetland sediments act both as sinks and sources of heavy metals, the monitoring of heavy metals is much needed to determine their overall functions (Khadka, 2011).

Groundwater-Surface Water Interactions in Wetlands

Groundwater and surface water interactions are an important link between the wetlands and the surrounding catchment areas (Fleckenstein et al., 2010; Schot & Winter, 2006). Such interactions help to understand the flow regime in and out of wetlands adjacent to agricultural fields. Because of varying seasonal weather patterns, many wetlands depend on a stable influx of groundwater (Winter et al., 1998). On the other hand, a stable inflow of surface water may also give rise to groundwater recharge.

Therefore, such interactions in wetlands would play an important role for the spatial and temporal availability of both surface water and groundwater in the environment (Schot & Winter, 2006).

Wetlands remain very sensitive to the function of the surrounding areas. Any change in the hydrological conditions is likely to affect the function of wetlands. For example, drainage of wetlands for agricultural or urban purposes could reduce their functioning capacity (Winter et al., 1998). Therefore, wetlands are sensitive to external stressors that could modify the groundwater flow regime. Also, because of this interaction, impacts on either of these components are likely to affect the water quality of the other.

There are various factors that influence the interactions between groundwater and surface water. Some of them include seasonal floods, rising water table, permeability, hydraulic gradient, and porosity of the aquifer materials. Because of the surface and groundwater interactions associated with other factors like precipitation and evapotranspiration, the water level fluctuates and determines the hydro-period of the wetland. Hydro-period refers to the amplitude and frequency of water-level fluctuations which affects all wetland characteristics, including the type of vegetation, nutrient cycling, and different aquatic habitats. Hydrology of wetlands (especially isolated wetlands) behaves differently in response to hydro-period, and the sustainability of such wetlands depends on their water supply exceeding losses due to evapotranspiration

(Winter et al., 1998; Schot & Winter, 2006). Figure 8 shows the diagrammatic representation of groundwater flow and its point of discharge.

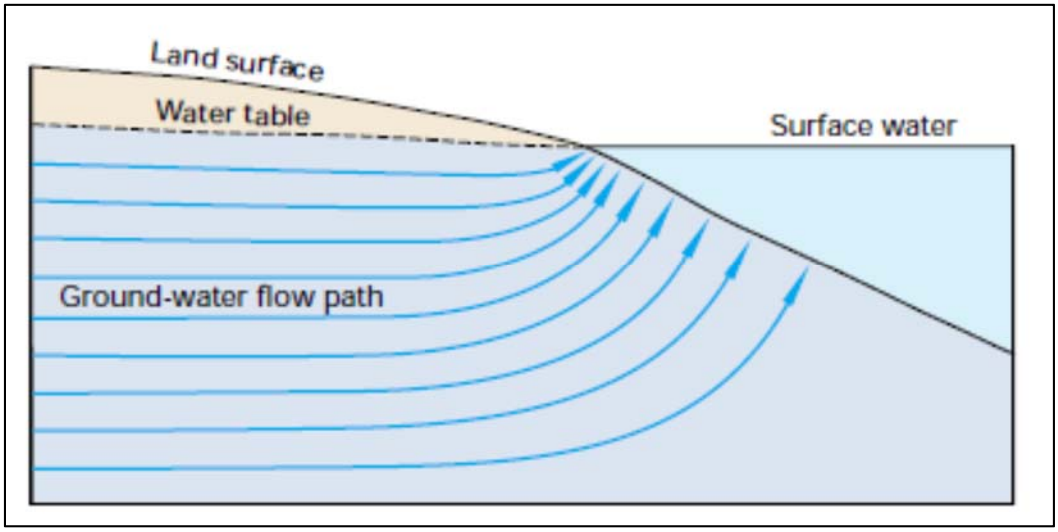


Figure 8: Diagram of groundwater flow to surface water
(Source: Winter et al., 1998)

When rain water falls on the ground, subsurface flow, both horizontal and vertical, takes place depending on the topography and soil characteristics. It is of prime importance to study the sub-surface flow in wetlands to understand how the system works. However, the direct measurement of such flow is difficult. A good way to measure such flow is by using various chemical tracers. The use of chemical tracers is popular because of their ready availability and convenience (USEPA & USGS, 1988). Some of the most commonly used chemical tracers are bromide, fluorescein, chloride, rhodamine WT, and various fluorocarbons (Davis et al., 1980). The use of tracers in the field of hydrology is highly recognized since these could be easily carried by water. They

give information concerning the direction or velocity of the water as well as potential contaminants transported in the system (Davis et al., 1980). Flury and Wai (2003) listed the following characteristics that make chemical tracers unique for experimental purposes:

- Conservative in nature (i.e., do not sorb on to soils, sediments, or rocks and usually flow with water without degradation over time)
- Background concentration is usually low
- Unaffected by changes in pH, alkalinity, ionic strength, or other chemical solutions
- Easily detectable by chemical analysis or by visualization
- Minimal toxicological impact on the study environment

Therefore, because of their unique characteristics, tracers are widely used to investigate subsurface water flow and the direction and velocity of groundwater movement (Davis et al., 1980; Flury & Wai, 2003). In order to investigate the sub-surface flow, this study had applied two chemical tracers; bromide (sodium bromide, NaBr) and fluorescein (sodium fluorescein or uranine, $C_{20}H_{10}O_5Na_2$). Application of such tracers is generally helpful to develop wetland restoration models (Stern et al., 2001).

Among many inorganic ions, bromide is widely used as an ideal tracer in the field of hydrology, in studies related to unsaturated zone flow paths and flow mechanisms in agricultural soils, movement of groundwater in irrigated fields, study of subsurface flow patterns in a sandy loam profile, etc. (Bosch et al., 1999; Gilley et al., 1990; Perkins et

al., 2011). Bromide, as a tracer, does its work effectively because of the following characteristics: (1) it has a very low background concentration ranging from <0.004 to 1.0 g $Br^{-}m^{-3}$ in rainwater and <0.01 to 0.3 g $Br^{-}m^{-3}$ in groundwater (Davis et al., 1980; Flury & Papritz, 1993); (2) it is rarely sorbed onto soil particles and it moves faster than the average water molecule (Flury & Wai, 2003); (3) it has a low background concentration in soil and it does not constitute a health and pollution problem in low concentrations (Gilley et al., 1990).

Fluorescein is widely used as a dye tracer to investigate flow characteristics of both surface water and groundwater. Fluorescein has a characteristic bright yellowish-green color with low toxicity in low concentrations (Davis et al., 1980). Some of the most commonly used fluorescein dyes as water tracers are uranine, sodium fluorescein, rhodamine WT, etc. (Flury & Wai, 2003). Although fluorescein dye adsorbs onto sediments significantly, several laboratory studies revealed that sorption is less likely to occur when the aquifer is characterized by materials like sand or sandstone. However, its sorption to media would impact its use as a conservative tracer (Gilley et al., 1990; Wolf, 2003). It could also undergo photochemical decay inducing rapid breakdown in the sunlight. It is sensitive to pH and under acidic condition (approximately<6), high adsorption onto sediments may occur (Davis et al., 1980; Wolf, 2003). Despite its disadvantages, the following are some advantages that make it an excellent water tracer: (1) it is water soluble and is highly detectable in low concentrations (strongly fluorescent); (2) it is inexpensive having good stability in natural water environment; (3) it is non-toxic to environment in low concentrations (Stern et al., 2001). Besides,

fluorescein is considered a unique water tracer because none of the other materials found in natural water is actually a part of the light spectrum (Stern et al., 2001).

CHAPTER 2

HYPOTHESIS AND OBJECTIVES

Wetlands have always been looked at as natural filters for various pollutants, which means filtering contaminants coming from the upland areas and discharging the clean water to the lowland water bodies. Because of their filtering capacity, today wetlands are considered as one of the important landscape features of the environment, and many efforts have been invested to protect the natural wetlands for their significant ecological functions. Because of rapid urbanization and advance agricultural practices, however, wetlands are acting more as a source of contaminants rather than a sink. Such activities have disturbed the natural balance of their ecological functions, thereby jeopardizing water quality. Therefore, studying the conditions of the existing wetlands as well as their performance in the environment could only be possible through conducting water quality monitoring.

Two hypotheses were proposed for this study. First, the wetland functions in filtering various contaminants coming from the surroundings. Second, there is sub-surface flow where the agricultural fields are generally expected to serve as the recharge area for the wetland.

The primary goal of this study was to determine the ecological function of the wetland in the environment. The other specific objectives include:

- To determine the water quality at different sampling sites of the wetland.
- To determine the changes of water quality at different sampling periods.

- To investigate the soil quality at different depths as well as sediments at different sampling sites of the wetland.
- To develop a water quality index (WQI) for the wetland.
- To investigate the sub-surface flow in and out of the wetland in order to understand the flow regime connecting the surrounding agricultural fields to the wetland.

CHAPTER 3

STUDY AREA

The study was conducted in the Beaver Valley Wetland, which is situated about 6.5 miles northwest of Cedar Falls in Black Hawk County, Iowa at the intersection of Beaver Valley Road and Union Road (Figure 9). It is a small, 63 acre reconstructed wetland. This wetland was restored by the Cedar Valley Wetlands and is maintained and managed by the Black Hawk County Conservation Board (Brown et al., 2005). Agricultural practice is mainly dominant at the south and the west side of the wetland.

The wetland serves as an important migratory waterfowl area for different bird and amphibian species. Some of the regularly observed species are pelicans, trumpeter swans, and numerous ducks and geese. Hunting is not allowed in the wetland and a permit (Appendix G) is required from the conservation board office to enter the facility (Mycountyparks, 2012). Sampling sites (Figure 9) are mostly located at the bank of the wetland starting from the north side, moving along the edges and ending at the east side of the wetland. Water usually remains stagnant without having much turbulence. When the water level gets high, the flow generally increases from the outlet and vice versa. During the summer of 2011 (study period), the wetland had good amount of water throughout the sampling season. However, during the summer of 2012, the wetland had significantly less water.

Figure 9: Map of the study area showing different sampling points (Map source: IDNR, 2011)

Climate

The study area is situated northwest of Cedar Falls in Black Hawk County where the climate is continental humid and is characterized by a wide variation in weather pattern and seasonal temperature. Summers are usually warm and humid, whereas winters are very cold with frequent snowfall and continuing snow cover.

The climate data provided in Table 5, and Figure 10 and 11 are derived and downloaded from the National Oceanic and Atmospheric Administration (NOAA) website (www.noaa.gov). Table 5 shows the monthly average temperature, precipitation, and snowfall during the study period. Based on the NOAA climatic report data for the year 2011, the coldest month was January with an average mean temperature of 13.6^{o}F and the warmest month was July with an average temperature of 77.6^{o}F. Extreme temperatures during the study year ranged from -21^{o}F to 99^{o}F. The precipitation ranged from 1.04 inches to 3.89 inches during the study period, and it started to increase from April onwards. Similarly, the amount of snow varied at different months showing snowfall of 12.3 inches in January.

Figures 10 and 11 show the comparison of average temperature and precipitation between previous years and the year of study. Figure 10 shows the average monthly temperature in different years. The temperature from May through November of the study year remained higher than in the previous years. Similarly, Figure 11 shows the monthly average precipitation for different years. It clearly shows that the average monthly precipitation in the study year was relatively less than other years.

Table 5: *Monthly average temperature, precipitation, and snowfall for the year 2011* (Source: NOAA, 2013)

Month	Temperature (ºF)	Precipitation (inch)	Snow (inch)
January	13.6	1.04	12.3
February	21.7	1.72	9.3
March	34	1.79	1.6
April	47.2	3.74	0.8
May	59.3	3.65	0
June	70	3.89	0
July	77.6	2.79	0
August	71.4	3.21	0
September	59.1	2.66	0
October	52.8	1.37	0
November	38.6	2.22	1.5
December	29.6	2.38	1.1

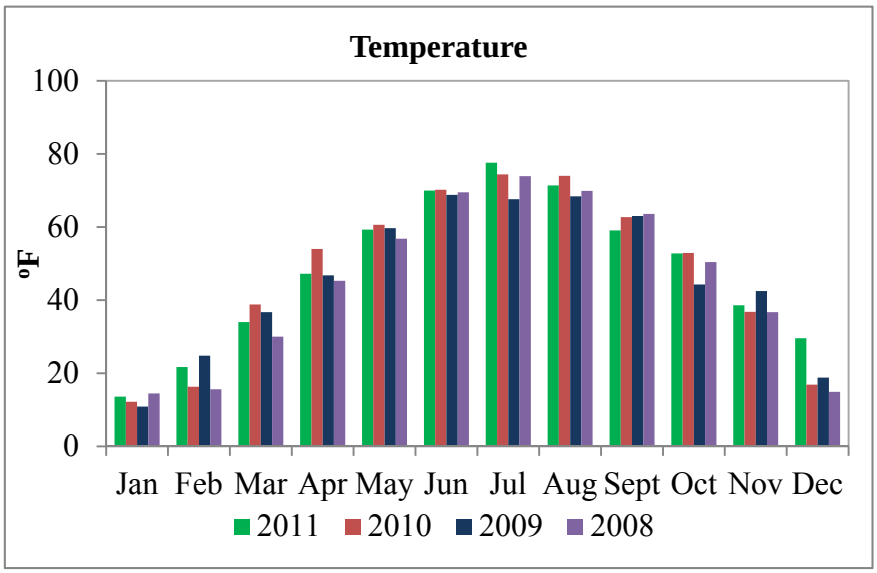


Figure 10: Monthly average temperature at different years

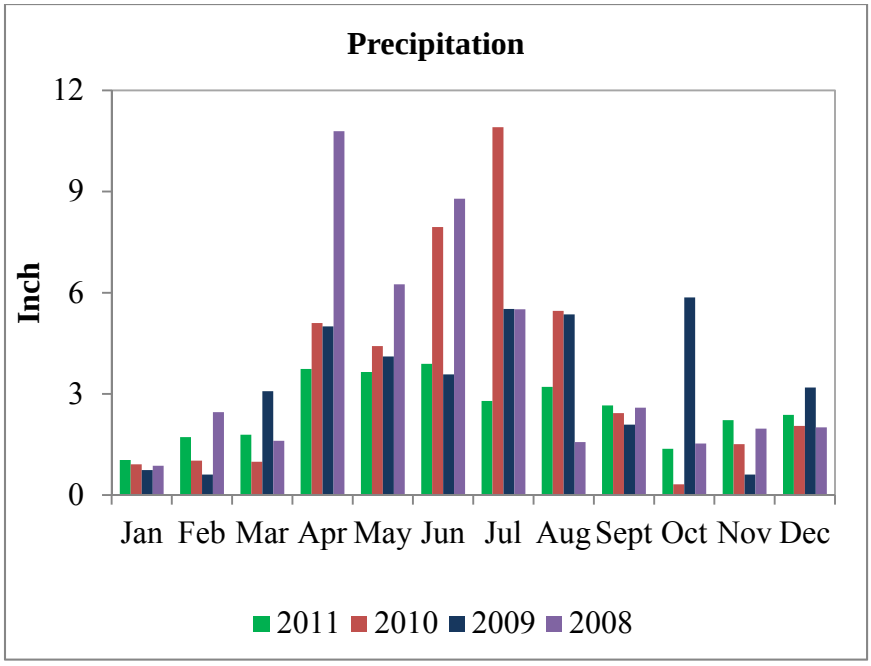


Figure 11: Monthly average precipitation at different years

Land Use

The Beaver Valley wetland is situated north of Cedar Falls, where agriculture is the major type of land use. The polygon digitization of land cover around the wetland is shown in Figure 12. Large agricultural lands are concentrated in the south and the west side of the wetland. The unit is situated in the intersection of Beaver Valley Road and North Union road. The other land use types include grasslands and forests.

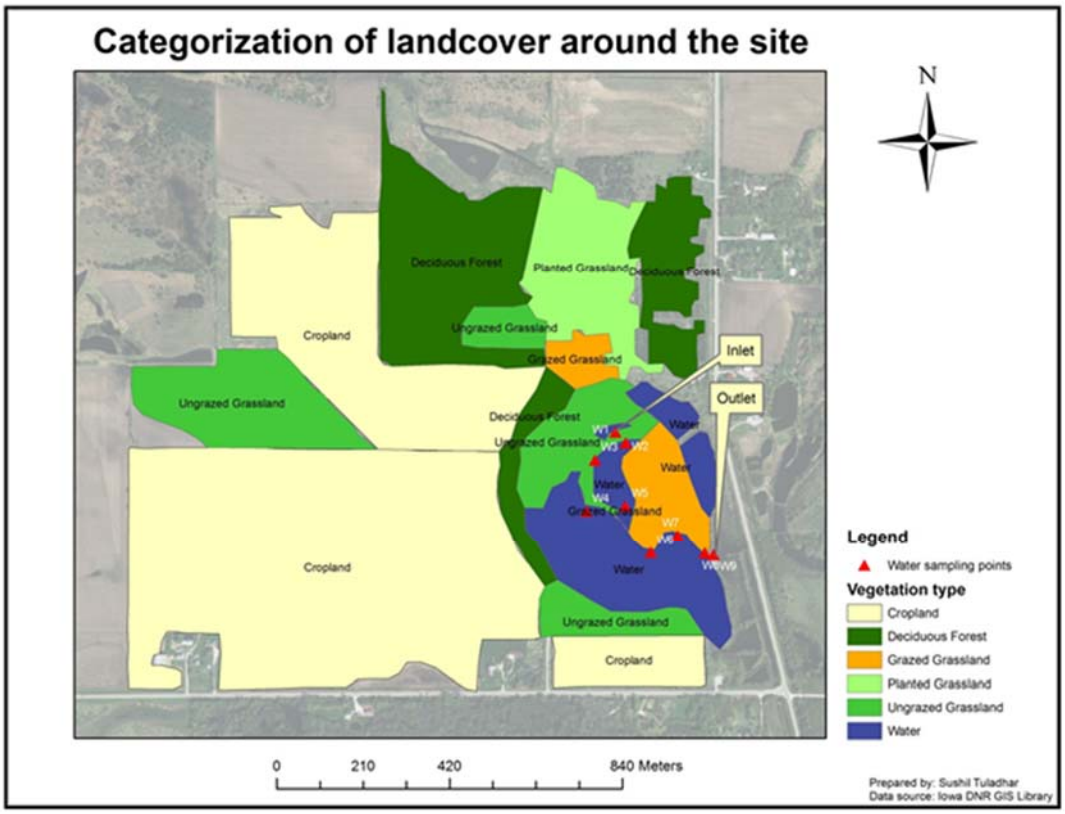


Figure 12: Categorization of land cover around the wetland

CHAPTER 4

MATERIALS AND METHODS

Sampling

The overall methodology of this study is provided in Figure 13. To assess the natural cycle of the Beaver Valley Wetland, water samples from 9 locations and soil samples from 14 locations within the wetland were analyzed. Samples were collected from May through August during the summer of 2011. The sites were numbered from W1 to W9 for water samples and S1 to S14 for soil samples. Soil samples were collected from different areas of the wetland representing the environment. The samples were collected with an interval of 21 days. After four months of regular sampling, it was extended for a couple of months in order to see how the water quality changes as the season changes. During the fall season, altogether 8 water samples were collected; 4 from previous sites (W1, W3, W6, and W8) and 4 additional samples from the other side of the wetland (W10, W11, W12, and W13). A total of 54 water samples and 84 soil samples were collected during the summer (May through August) and 24 water samples were collected during the fall (September through November). The sampling dates were defined as early summer (May 5, June 1, and June 22), mid-summer (July 15, July 31, and August 26), and late summer (September 23, October 14, and November 5). After collection, the samples were temporarily stored in an ice-packed cooler in order to protect them from excessive heat. On site testing was done for pH, temperature, conductivity, total dissolved solids (TDS), turbidity, and dissolved oxygen (DO). Subsequently, the samples were brought back to the Hydrology Lab and the Environmental Biology

Research Lab at the University of Northern Iowa (UNI) for further analysis. In the lab, the water samples were analyzed for nitrate, chloride, sulfate, biochemical oxygen demand (BOD), total suspended solids (TSS), and total phosphorus. The soil samples were analyzed for heavy metals and total phosphorus.

To study the sub-surface flow of water toward the wetland, six temporary monitoring wells were constructed and were used for dye tracing experiments.

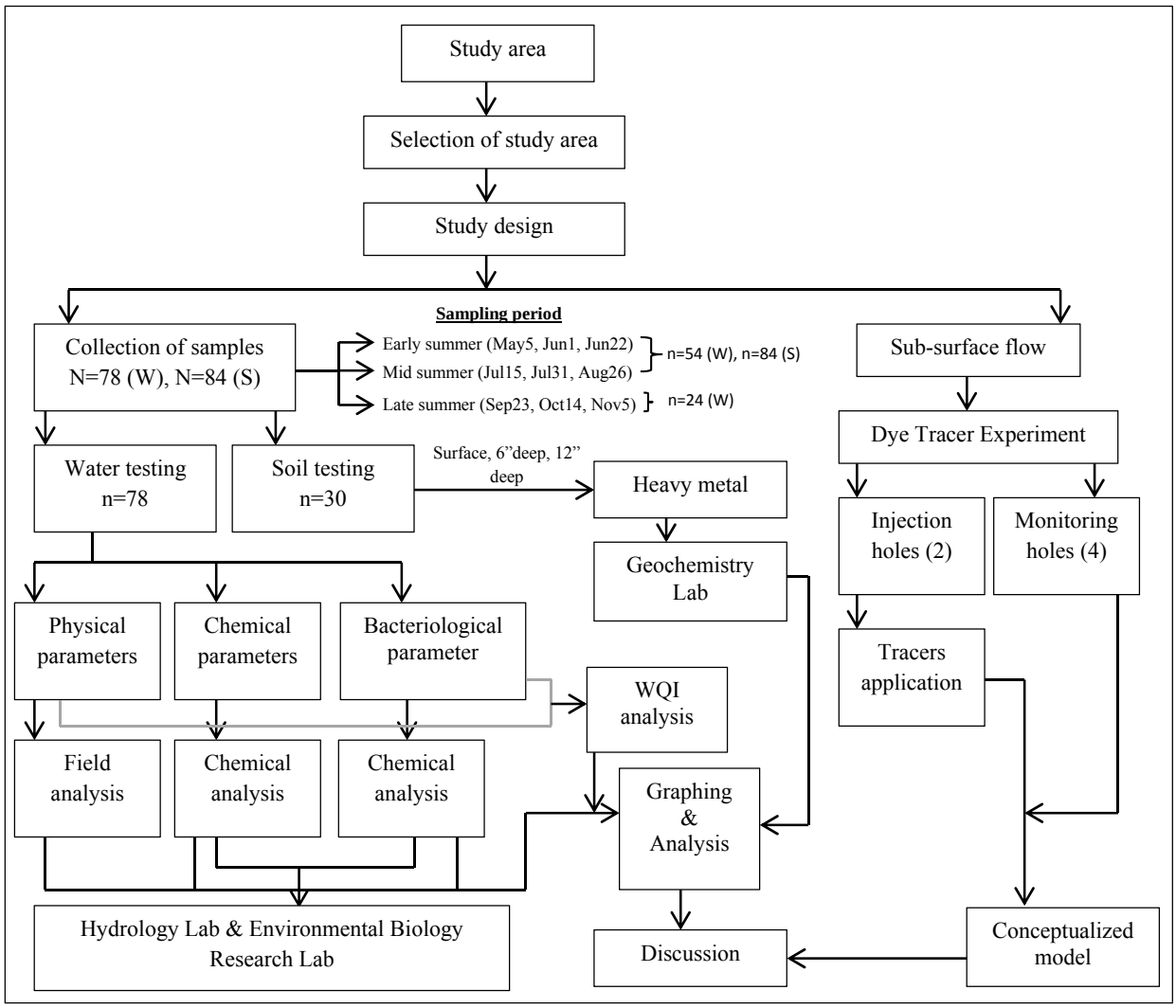


Figure 13: Flow diagram showing the overall methodology

Field Methods and Instruments

Two sterile HDPE (High Density Polyethylene) plastic bottles for each site for chemical parameters, 1 liter size plastic bottles for TSS, and glass bottles for BOD test were arranged for the sampling. The water samples were collected carefully as much as possible avoiding any physical disturbance to the water. These samples were later refrigerated at 4^{o}C in the Environmental Biology Research Laboratory at UNI.

Table 6: *Field equipment used for their corresponding parameters*

pH	EXTECH pH meter
Electrical conductivity, TDS, Temperature	HANNA EC/TDS meter
DO, DO percent saturation	HACH HQ 30d meter with LDO probe
Turbidity	LaMotte 2020 Turbidity meter

Several of the water quality parameters were immediately measured at the field using basic equipment like pH meter, conductivity meter, turbidity meter, and DO meter (Table 6 & Figure 14). The measured parameters at the field were pH, temperature, electrical conductivity, TDS, DO, DO percent saturation (DO%), and turbidity.

All these instruments were calibrated prior to field measurements. While taking measurements, instead of dipping the instruments directly into the water, samples were collected in a plastic container. pH, temperature, electrical conductivity, and TDS were measured by dipping meters into the plastic container. For turbidity, the water sample was collected and filled to the marked line in a small glass vial and then was measured

with a LaMotte turbidity meter. DO and the percent saturation of DO were measured directly by immersing the DO meter into the surface water body.

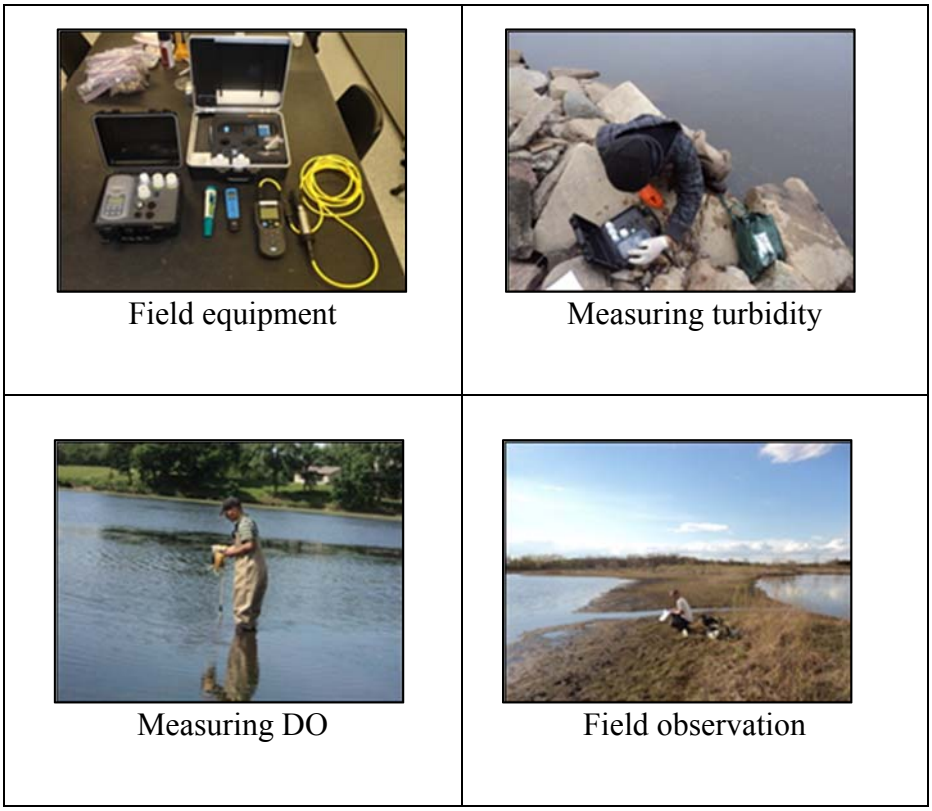


Figure 14: Basic field equipment and conducting field activities

The soil samples were collected using a soil probe and in some cases using a hand trowel (Figure 15). The soil probe was primarily used to collect the samples from around the wetland whereas the hand trowel was used for some spot sampling from the wetland base. Soil samples were collected from three different depths namely surface soil, 6 inch deep soil and 12 inch deep soil. Later these samples were stored in a cooler at 4^{o}C in the Environmental Biology Research Laboratory at UNI.

Soil profile

Soil sample collection

Figure 15: Soil sample collection

Laboratory Analysis

The rest of the parameters like total suspended solids (TSS), *E. coli*, ammonia, total phosphorus, chloride, nitrate, sulfate, and heavy metals were analyzed in the Hydrology Lab and the Environmental Biology Research Lab at UNI.

Total Suspended Solids

TSS was measured in the filtration manifold setup in the Hydrology Lab (Figure 16). Glass fiber prefilters made by Millipore (pore size of 0.7 µm; filter diameter of 47 mm) and a filtration manifold were used for this purpose. Using the vacuum pump, a measured amount of water sample was filtered through a pre-weighed filter paper. After the filtration was complete, the funnel was rinsed with DI water and the filter paper was oven dried at 60^{o}C to get rid of the moisture and then weighed again. The difference in the weight of the filter paper before and after the filtration gave the mass of TSS in the

given volume of water sample. The final unit for TSS was expressed in milligrams per liter (mg/L). For TSS analysis, the volume of filtered water was mostly above 500 ml to maintain accuracy of measurement. However, high amount of suspended solids in some of the samples clogged the filter papers before achieving that volume thus limiting the sample volume to less than 500 ml. In such cases, whenever possible, highly turbid water samples were run through two different filter chambers at a time.

Figure 16: Filtration manifold

Escherichia coli

Coliscan Easygel method was used to analyze *E. coli* in the water samples. This method, a patented product of Micrology Laboratories, is an easy way to identify and count the number of *E. coli* as well as the total coliform count in water samples. It contains a sugar linked to a dye, which when acted upon by certain enzymes produced by *E. coli* and coliforms, produces distinct purple and pink colors. This determines the presence of *E. coli* and other coliforms in the water (Micrology Laboratories, 2012). First

of all, water samples at the field were collected carefully after rinsing the bottles out once or twice with the same water. In the lab, a known volume of samples (e.g., 5 ml) was carefully transferred into the medium and swirled well to distribute the inoculum (Figure 17). Then it was poured into the labeled petri dishes and swirled gently until the dish was uniformly covered with liquid. Then the dishes were set on the lab bench for 40 minutes to let it solidify. When solidified, the dishes were placed right-side-up directly into an incubator at 35ºC for 24 hours. The final number of *E. coli* was determined by counting only the purple colonies, usually expressed in colony forming unit per 100 ml (CFU/100 ml).

Coliscan Easygel and electronic pipette

Pouring media into petri plate

Figure 17: Easygel Coliscan method

Biochemical Oxygen Demand

Biochemical Oxygen Demand was measured in the lab. For this, water samples were collected carefully in the BOD bottles by immersing the bottle below the water

surface. The container was securely capped avoiding the exchange of air between the bottle and the atmosphere. The bottles were brought back to the lab and were stored in the dark for 5 days. Subsequently, the DO at day 5 was measured. Then the difference between the initial DO and the day5 DO gave the BOD which is expressed in mg/L.

Anion Species

The anion species like chloride, nitrate, phosphate, sulfate, and bromide were determined with a Dionex (Model DX-120) ion chromatograph under suppressed conductivity (Figure 18). Ion elution was accomplished using a CO_3-HCO_3 solution. Before analyzing the samples, deionized water was injected to verify the stability of the machine. Flow rate was set at 1.95 mL/min. Known standards of the target ions (5, 25, 50 ppm) were used for machine calibration, and a separate 25 ppm standard solution was used to check the validity of calibration. The unknown samples were poured into 5 mL plastic vials fitted with 20 micron filter caps and then loaded into an AS40 automated sampler for injection into the system. The samples flowed from the injection loop first to the guard column (AG14) and then to the anion exchange column (AS14), and finally to the ASRS 300(4 mm) suppressor to complete the cycle. The peak retention times were 1.36 minutes for fluoride, 1.74 minutes for chloride, 2.60 minutes for nitrate, 3.40 minutes for phosphate, and 4.02 minutes for sulfate. Sample scan, data acquisition, and statistical analysis were done by Chromatography Management System (CMS) software called “Chromeleon” (released from Dionex). The analytical margin of error was ±0.5 ppm.

Autosampler and Dionex DX-120 Ion Chromatograph

Dionex DX-120 Ion Chromatograph unit

Figure 18: Dionex DX-120 Ion Chromatograph

Ammonia

Ammonia was analyzed by the salicylate method, which was run through DR-850 Colorimeter. For each sample, two AmVer Diluent Reagent vials were taken. Two ml of sample was added to one vial and 2 ml of deionized water was added to the other vial as a blank. Using a funnel, the content of one Ammonia Salicylate Reagent Powder Pillow was added to each vial. Then, the content of one Ammonia Cyanurate Reagent Powder Pillow was added to each of them. The vials were tightly capped and then mixed thoroughly to dissolve the powder. Usually, a green color develops if ammonia is present in the water. In the colorimeter, a 20-minute reaction time was set, which allowed the samples to complete the reaction. For the blank, the ZERO button was pressed and then the samples were measured.

Total Phosphorus

The concentration of total phosphorus both in the water samples and sediment samples was determined in the laboratory following the method given in Standard Methods for the Examination of Water and Wastewater (Clesceri et al., 2005). The detailed procedure of this method is given in Appendix F. The complete analysis involved two stages; the persulfate digestion method and the ascorbic acid assay method.

Water. A total of 78 water samples were run for the determination of total phosphorus. In the process, a standard phosphorus solution of 50 µg PO_4^{3-}-P was prepared as a stock solution. For this, 219.5 mg of anhydrous potassium phosphate monobasic (KH_2PO_4) was mixed to 1 L of deionized water. Using this stock solution, depending on the expected range of phosphorus in the samples, standards of 0, 10, 25, 50, 75, 100, 125 µgP were prepared with deionized water in 50 ml of volumetric flasks (Table 7).

Table 7: *Phosphorus standards used during phosphorus analysis in water*

Concentration (µgP)	**Volume used from the stock solution (ml)**
0	0.0
10	0.2
25	0.5
50	1.0
75	1.5
100	2.0
125	2.5

In the persulfate digestion method, the first step involved the conversion of all of the phosphorus in the sample to orthophosphate. Specifically, 50 ml of each sample were added to 125 ml Erlenmeyer flasks. Then, 1 ml of sulfuric acid (H_2SO_4) solution and 0.4 g of ammonium persulfate [$(NH_4)_2S_2O_8$] were added to each sample in the flask. These flasks were covered with aluminum foil and autoclaved for 30 minutes. After the samples were cooled, 1 drop of phenolphthalein indicator solution was added to each flask and 1N sodium hydroxide (NaOH) was then added to neutralize to a faint pink color. The standard solutions were also treated similarly as samples. The samples and standards were transferred into 100 ml volumetric flasks and filled up to the mark with deionized water.

Glassware ready for phosphorus analysis

Samples in blue color indicating the presence of phosphorus

Figure 19: Phosphorus analysis

In the ascorbic acid assay method, the digested samples and standards were reacted with mixed reagent called Murphy-Riley Mixed Reagent. This reagent was

prepared by mixing 125 ml of 4N H_2SO_4, 12.5 potassium antimony tartrate solution, 37.5 ml of ammonium molybdate solution, and 1.06 g ascorbic acid in a 250 ml volumetric flask with deionized water. Now, 10 ml of mixed-reagent was transferred to 50 ml of volumetric flasks, and then 40 ml of the samples and standards (prepared in the first method) was added to each flask. These were allowed to react for 20 minutes until the reaction gave an intense blue color (as shown in Figure 19), whose intensity was measured through a GENESYS^{TM} Spectrophotometer set at the wavelength of 880 nanometers. The absorbance reading of the standard solutions was plotted to make calibration curves based on which the total phosphorus concentration in the samples were determined. The samples were replicated until the standard deviations were obtained below 25%.

Sediments. Similar to the water samples, the total phosphorus in the sediments was also measured. In this case, since soil samples have relatively higher amount of phosphorus than in water samples, appropriate concentration of phosphorus standard solutions were prepared from the stock solution such as 0, 50, 100, 250, 500, 750, 1000 µgP (Table 8).

Table 8: *Phosphorus standards used during phosphorus analysis in sediments*

Concentration (µgP)	**Volume used from the stock solution (ml)**
0	0.0
50	1.0
100	2.0
250	5.0
500	10.0
750	15.0
1000	20.0

In the persulfate digestion stage, soil samples were oven dried at 105ºC for 24 hours to get rid of all the moisture content in soil. Then 1.5 g of dry sample was added to 50 ml of deionized water in 250 ml Erlenmeyer flask. After digesting the samples, the solutions were transferred into 50 ml centrifuge tubes and centrifuged at 4000 rpm for 10 minutes. The supernatants were then transferred to 100 ml volumetric flasks. The rest of the procedures were done similarly as for the water samples.

Water Quality Index Calculation

Although Water Quality Index (WQI) is determined considering nine parameters, in this study WQI was calculated using only eight parameters. These parameters are dissolved oxygen (i.e. dissolved oxygen saturation), fecal coliform, pH, biochemical oxygen demand, total phosphate, nitrate, turbidity, and total dissolved solids. The factor of temperature change was not included for WQI because the study area is small enough to make this factor insignificant. According to Boulder Area Sustainability Information

Network (BASIN) (2005), if certain parameters could not be included, the overall WQI can be obtained by dividing the WQI (considering the included parameters) by the sum of the weighting factors.

In this study, quality index (QI) was first determined from the respective graphs for each parameter based on the test results. Then, their individual WQI was calculated as the product of weight factor (w) and quality index (QI). Finally, the overall WQI was calculated by dividing the water quality indices by the total weight. The illustration of WQI for one of the sites (i.e., W4) is presented in Table 9.

Table 9: *Calculation of WQI*

Parameter	**Test Result**	**Weightage Factor (w)**	**Quality Index (QI)**	**WQI (w x QI)**
DO (% saturation)	97.6	0.17	99	16.83
E. coli (CFU)	80	0.16	47	7.52
pH	7.66	0.11	91	10.01
BOD (mg/L)	3.29	0.11	65	7.15
Temperature change (^{o} C)	n/a	0.1	-	-
Phosphate (mg/L)	0	0.1	100	10
Nitrate (mg/L)	0	0.1	97	9.7
Turbidity (NTU)	11.42	0.08	73	5.84
TDS (mg/L)	39.57	0.07	86	6.02
	Total	**0.9[a]**		**73.07[b]**
Final WQI				**81.18[c]**

[a] $\sum w$; [b] $\sum(w \times QI)$; [c] $\sum(w \times QI)/\sum w$

n/a − Data not available. The temperature change was not included in WQI calculation.

Dye Tracer Experiment

Dye tracers are applied in different environmental settings like aquifers, streams, rivers, estuaries, reservoirs, lakes, and wetlands mainly to study flow rates and preferential flow paths of surface water and groundwater (Dierberg & DeBusk, 2005). In this study, the dye tracers were used to investigate the subsurface flow in and out of the wetland. The primary goal was to understand the flow regime connecting the surrounding agricultural fields to the wetland. The agricultural fields are generally expected to serve as the recharge area for the wetland.

An area on the southern end of the wetland was chosen with an assumption that the flow was toward the wetland (shown with dotted arrow in Figure 20). Six injection holes were dug using an Earthquake Viper Auger Machine with the appropriate auger bit (Figure 22). The holes are approximately 2 feet deep. Out of the six holes, two were used as injection holes and the remaining four were used for monitoring tracer migration (Figure 21). The monitoring holes were drilled based on the assumption that the prevailing flow field was from the injection holes to the lake further south of the area. Any tracer moving in the subsurface was expected to be captured in the monitoring holes.

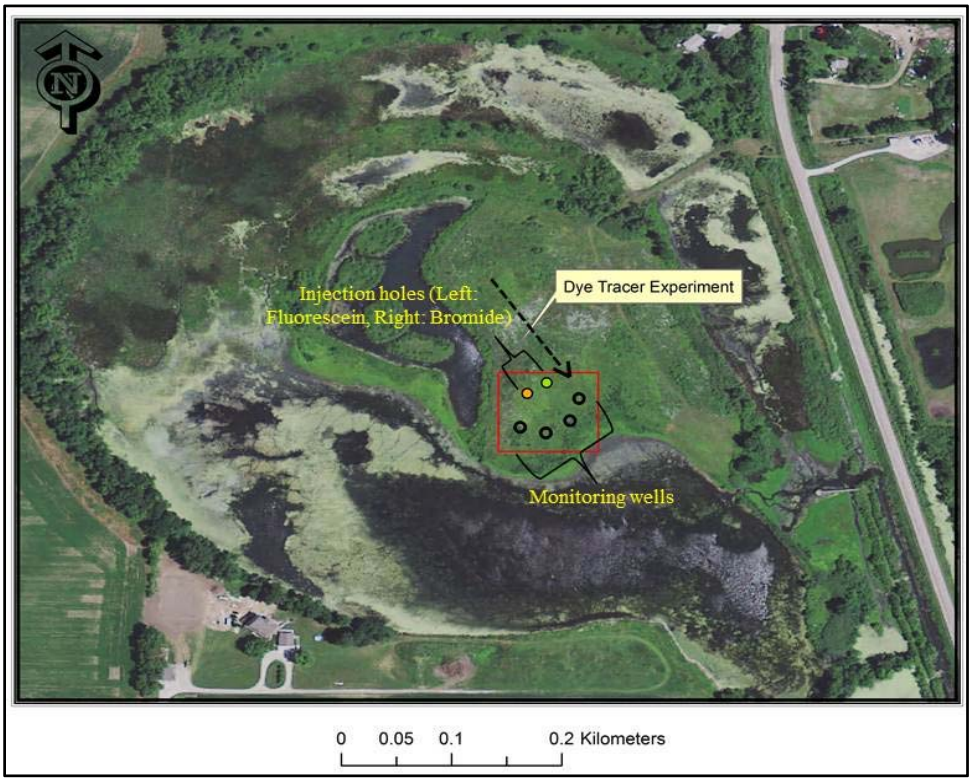


Figure 20: Map view of Dye Tracer Experiment

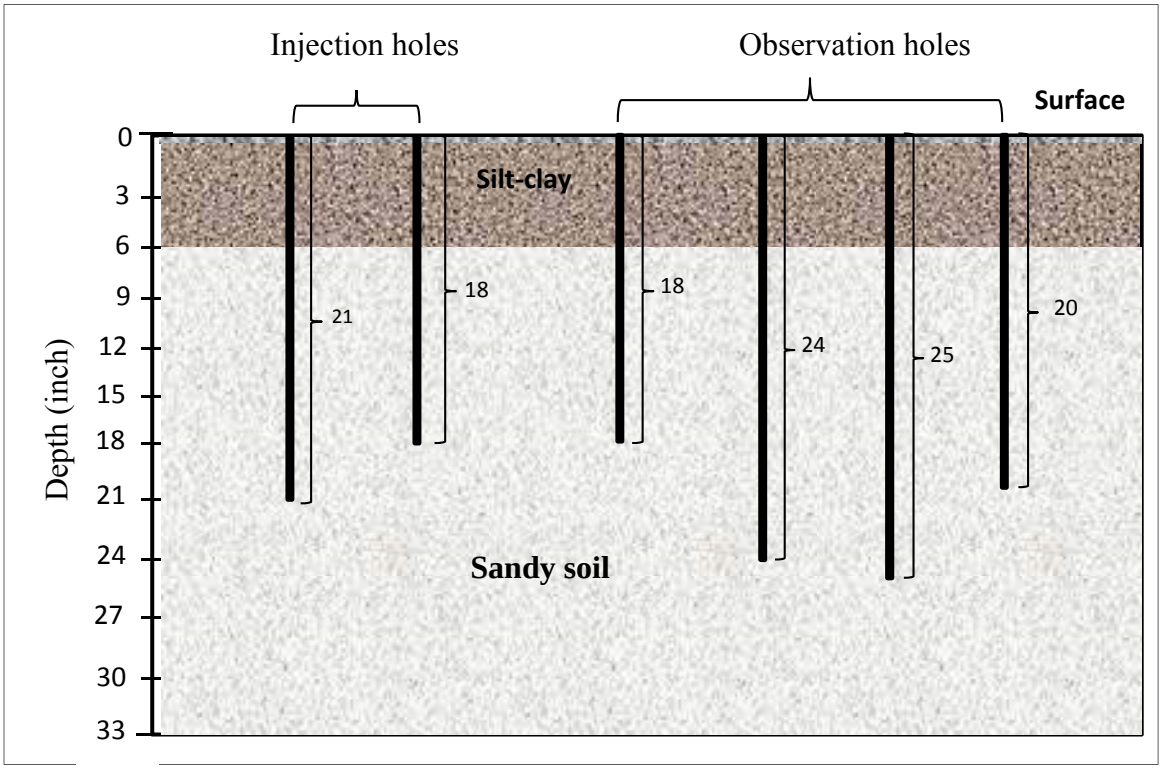


Figure 21: Schematic one-dimensional diagram for auger hole

To perform the dye tracer experiment, fluorescein dye ($C_{20}H_{10}O_5Na_2$; CAS: 518-47-8) and sodium bromide (NaBr; CAS: 7647-15-6) were selected as the tracers. Appropriate solutions of these tracers were prepared in the laboratory. About 10 g of fluorescein was mixed in 1L of deionized water (DI) to prepare the fluorescein dye and approximately 10 g of bromide was mixed in 1L of DI water to prepare the bromide dye. These solutions were added in the injection wells separately (as shown in Figure 22). The holes were covered with cement slabs to avoid the influence of direct rainwater and runoff from the surrounding areas.

On the day of injection, water samples were collected every 2-3 hours (from 10 am until 8 pm) from the monitoring wells. The next day, the water samples were collected every 4 hours (from 8 am until 8 pm). On the third day, water samples were collected at three different times; one set at 8 am, one set at 12 pm, and the final set at 8 pm. The samples were stored and refrigerated in the lab for subsequent chemical analysis. As a special measure, extra samples were collected following rain events.

Earthquake auger machine

Drilling hole

Auger hole

Injecting fluorescein dye

Figure 22: Equipment and different steps during dye tracer experiment

Fluorescein Analysis

In the lab, Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as the light source was used to analyze fluorescein. During the analysis, the excitation wavelength, the sampling interval, and the slit width were set at 350 nm, 0.2 nm, and 5 nm respectively. In a study by Aley (2008), the acceptable emission wavelength for fluorescein in water ranged from 508 to 511.7 nm. The emission wavelength range for this study was set from 250 to 750 nm to ensure detection. About 3 ml of the water sample was put in a disposable polystyrene cuvette and placed in the RF-5301 machine. The machine is controlled by a programmable computer (Aley, 2008). All the water samples were scanned for fluorescein. For bromide, the water samples were analyzed by Ion Chromatograph (see anion section for details).

Heavy Metal Analysis

The analysis for heavy metals was performed in the Geochemistry Lab at UNI by using a PANalytical MiniPal 4 XRF (X-Ray Fluorescence) Spectrometer (Figure 23). The heavy metals analyzed were arsenic (As), cobalt (Co), cupper (Cu), chromium (Cr), cadmium (Cd), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn).

PANalytical MiniPal 4 XRF Spectrometer

SPEX 8000 Mixer/Mill

Figure 23: XRF Machine

First of all the soil samples were oven dried at 30ºC for couple of days to eliminate the moisture content in the soil. After drying, when necessary, the samples were sieved to remove any small wood twigs and dried grasses. Then sets of samples were pulverized for 10 minutes in a SPEX 8000 Mixer/Mill (Figure 23). Using 3526-Ultralene Window Film (4 µm thick; 64 mm diameter) as a sample window, the pulverized samples were carefully placed and leveled in XRF Sample Cups and run through the spectrometer.

Application of Geographic Information System and Data Analysis

Geographic Information System (GIS) is an integrated system of computer software, hardware, and spatial data (geographically referenced) along with its attributes in order to map, analyze, and visualize real world problems. The use of GIS helps in

understanding and interpreting the data. In this study, ESRI's ArcGIS 10 was used to map and analyze the distribution of water quality data.

The results of the various water quality parameters and heavy metals were analyzed and compiled by using line and bar graphs in Microsoft Excel. Data were analyzed by a standard statistical procedure using JMP10 and S-Plus software. Univariate analysis was used to calculate mean, standard error, minimum, maximum, range, and standard deviation. Bivariate analysis (correlation and ANOVA) was used to examine the relationships between the variables.

CHAPTER 5

RESULTS AND DISCUSSION

The study was conducted from May 5 through November 5 of 2011. Out of 78 water samples collected, 75 were used for physical, microbiological, and ammonia analysis. Three additional sites were identified later for detailed investigations. Similarly, out of 84 soil samples collected, 30 were processed for heavy metals and phosphorus analysis.

Physical Water Quality Parameters

pH

In aquatic ecosystems, pH affects many chemical and biological processes (USEPA, 1997). According to Water Quality Guidelines for Wetlands prepared by Washington State Department of Ecology in 1996, it states that in wetlands, chemical process such as ammonia volatilization (i.e., removal of nitrogen from wetlands) occurs at high temperature and at a pH of greater than 7.5. Likewise, when the pH of water tends to be more acidic it can reduce the wetland's ability to process nitrogen and phosphorus. Organisms have various levels of pH tolerance. A range of 6.5-8.0 is preferred by the largest variety of aquatic animals (USEPA, 1997). On one hand, pH outside this range reduces the physiological systems of most organisms, whereas on the other hand it shows effect on the algal abundance. Many studies show that algal abundance increases as the pH lowers and vice-versa (Bergstrom et al., 2007).

Table B1 in Appendix B shows the pH of water samples ranging from a minimum of 6.14 to a maximum of 10.91 with an average value of 8.45 ± 0.14. Most of the pH values are above 8 (Figure 24), which means that the water is slightly alkaline. The average pH peaked on June 1, gradually decreasing over mid-summer, and again increasing during late summer. There are various factors that might determine the change of pH in the aquatic ecosystem. Among them, geological settings such as rock types, photosynthesis, and decay processes could be some of the factors that might change the pH level. During the process of photosynthesis, it usually consumes hydrogen molecules thereby reducing the concentration of hydrogen ions and causing pH to rise. Likewise, during the fall season, when leaves fall off on the water, the decomposition or decay process predominates. These processes consume oxygen and release carbon dioxide, thereby decreasing pH value.

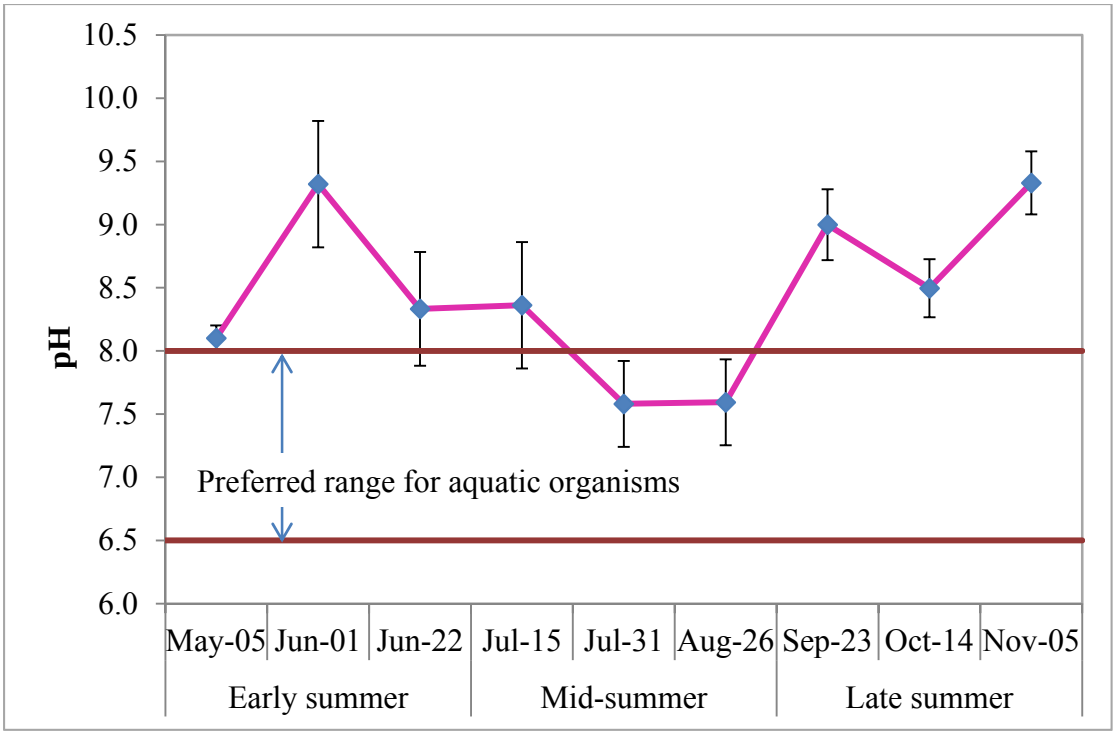


Figure 24: Variations of average pH at different sampling periods

Temperature

Temperature is an important factor that can have major influence on the biological activity of aquatic life. Temperature can also impact the rate of chemical reactions. For example, when the temperature of water increases, DO decreases. As a result, low DO makes aquatic animals suffer and put them in stress. The most obvious natural cause for the variation in surface water temperature is due to change in seasonal ambient air temperature. This study clearly shows the strong correlation between the average ambient air temperature and the average water temperature throughout the sampling period (Figure 25; R^2=0.944).

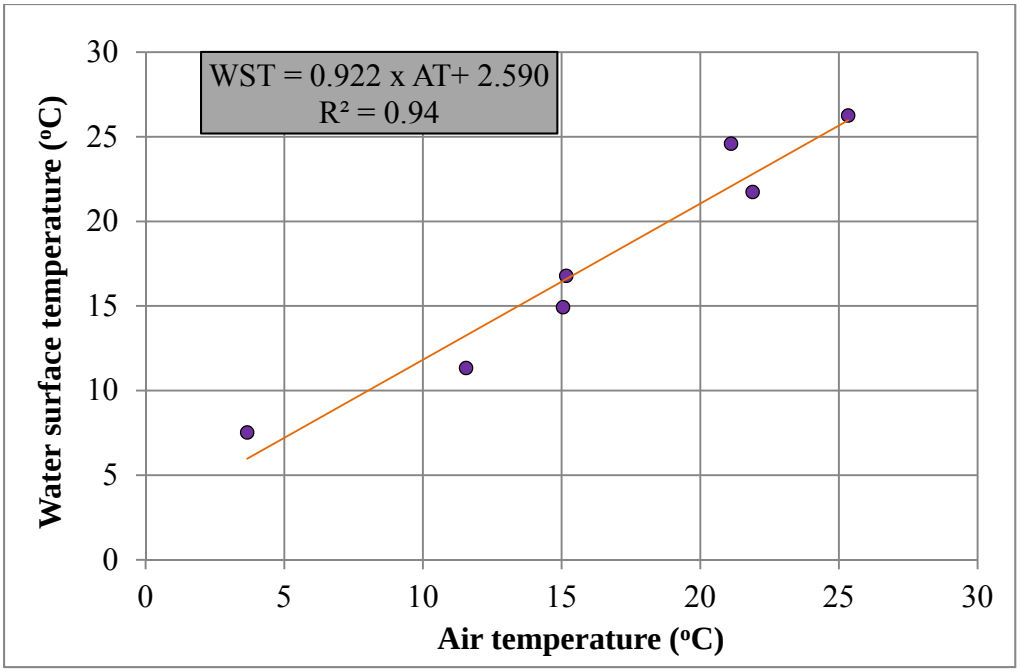


Figure 25: Correlation between average ambient air temperature and average water temperature

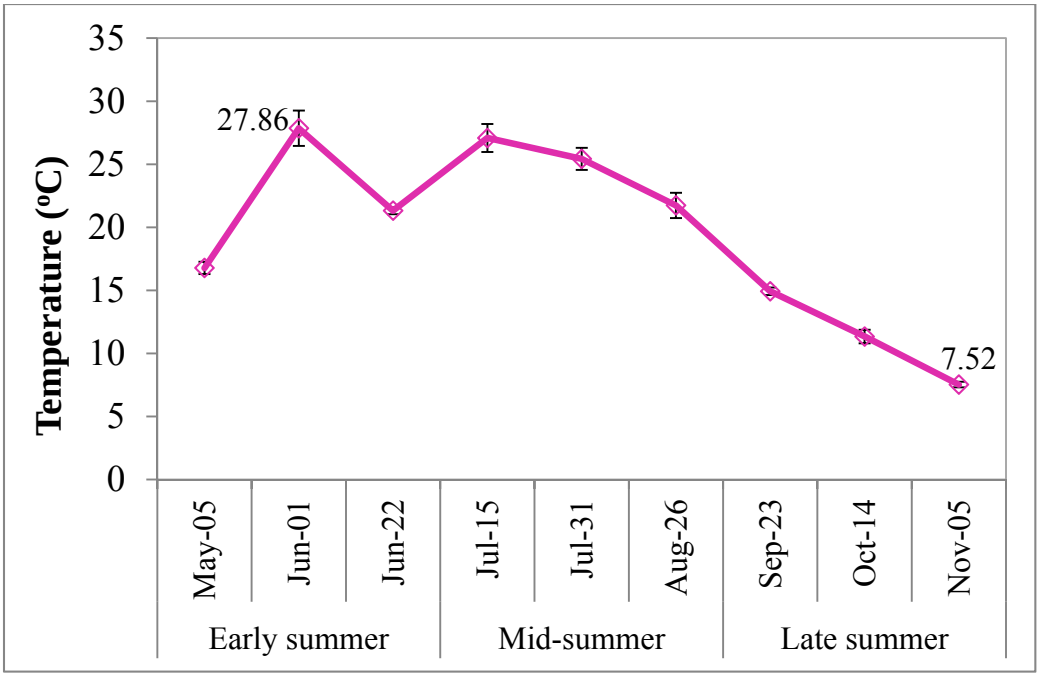


Figure 26: Variations of average surface water temperature at different sampling periods

During the study, the surface water temperature ranged from a minimum of 6.80^{o}C to a maximum of 33.9^{o}C. The average water temperature was found to be 19.75 ± 0.83^{o}C (Table B1, Appendix B). Figure 26 shows the average distribution of temperature during the study period. It reveals that the surface water temperature remained high at 27.86^{o}C during early summer. Then the temperature started declining from mid-summer onwards and was found to be the lowest at 7.52^{o}C in late summer.

Electrical Conductivity and Total Dissolved Solids

Electrical conductivity is defined as the measurement of the ability of water to pass an electric current. The presence of high inorganic dissolved solids such as nitrate, chloride, sulfate, phosphate, calcium, carbonate, bicarbonate, magnesium, and sodium in the water will increase the conductivity of the water (USEPA, 1997; Galbrand et al., 2008). It could also be affected by high surface water temperature. Conductivity of water bodies such as wetlands, rivers, and streams also depends on the geology of the area (USEPA, 1997). The preferential range of the conductivity for certain species of aquatic animals such as fishes and invertebrates is from 150-500 µs/cm (USEPA, 1997).

Since conductivity is dependent on dissolved inorganic materials, it is also a function of total dissolved solids (TDS). TDS is defined as a measure of dissolved constituents in a given volume of water including minerals, salts or metals. Although TDS is not a health hazard parameter, its presence at an elevated level in the water might indicate high levels of other chemical constituents. In addition, excessive TDS can reduce water clarity, hinder photosynthesis, and lead to increased water temperatures (Galbrand et al., 2008). To date, 27 states have enacted criteria for TDS according to site or

watershed conditions in order to protect aquatic life. However, such criteria for the protection of aquatic life have only been developed for 15 of the 27 states, and vary widely from state to state (IDNR, 2009). For example, Alaska, Mississippi, Oregon, Illinois, Indiana, and Louisiana have a criteria of 1000 mg/L, 750 mg/L, 100 mg/L, 1500 mg/L, 750 mg/L, 500 mg/L respectively for the protection of aquatic life and other designated uses (IDNR, 2009; USEPA, 2001c). In case of Iowa's lakes or streams, the general criterion set for TDS is 750 mg/L in order to protect the aquatic life (IDNR, 2009).

In this study, the conductivity and TDS were within the range of water quality standards (Table A1, Appendix A). The study shows that the conductivity value ranged from 162-442 µs/cm with an average of 261.02 ± 9.11µs/cm. On the other hand, the TDS ranged from 104-305 mg/L with an average of 179.68 ± 6.23 mg/L (Table A1 & B1, Appendix A & B). The average distribution of conductivity shows that the value was higher during mid-summer than in the other sampling periods (Figure 27). This is due to the fact that the water level dropped during mid-summer, making the dissolved substances more concentrated (Azous & Horner, 1997). The maximum TDS level of 305 mg/L was found during mid-summer (site W3 on June 1), whereas the minimum TDS level of 104 mg/L was found during late summer (site W12 on September 23).

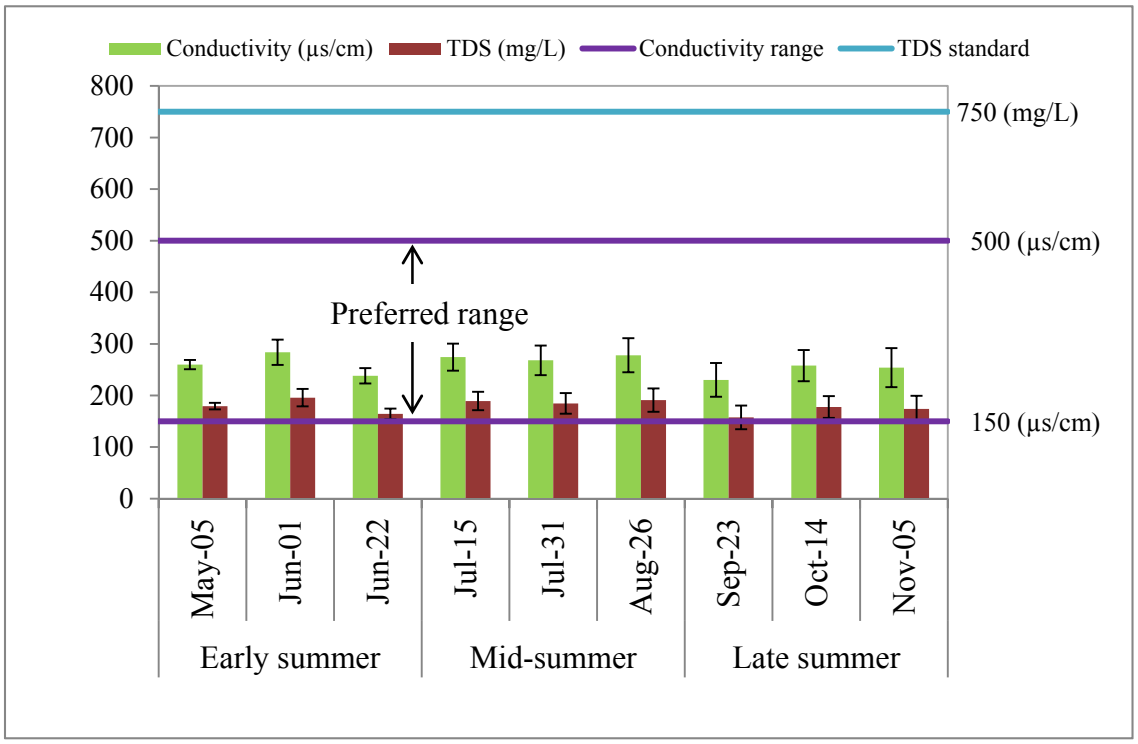


Figure 27: Variations of average electrical conductivity and TDS at different sampling periods

Turbidity and Total Suspended Solids

Turbidity measures the clarity of water. The obvious reasons for causing turbidity in water are suspended particles (essentially clay particles), plankton (microscopic plants and animals), sediment runoff, re-suspension of bottom sediments, and wind velocity. High turbidity alters the chemical and biological activities in the water. For example, high turbidity increases the water temperature by absorbing more heat, thereby making the water warmer. This, in turn, reduces the DO concentration stressing the aquatic life. Similarly, high turbidity also obstructs the amount of light penetrating the water surface, reduces the photosynthetic process and the DO level (USEPA, 1997). Total Suspended

Solids (TSS), on the other hand, measures the amount of suspended particles in the water. TSS includes any suspended solids such as clay, silt, fine particles of organic matter, inorganic particulates such as iron, soluble colored compounds, and phytoplankton that remain suspended in water over a long period of time and do not pass through a filter (Galbrand et al., 2008). TSS is considered as a major water quality concern because of the following reasons: (i) obstructs light penetration in water reducing photosynthetic process, (ii) reduces the water depth due to sediment deposits, (iii) oppresses the growth of aquatic vegetation, habitat, food, macro and microorganisms, and (iv) absorbs heat increasing the water temperature and decreasing the DO level (Galbrand et al., 2008).

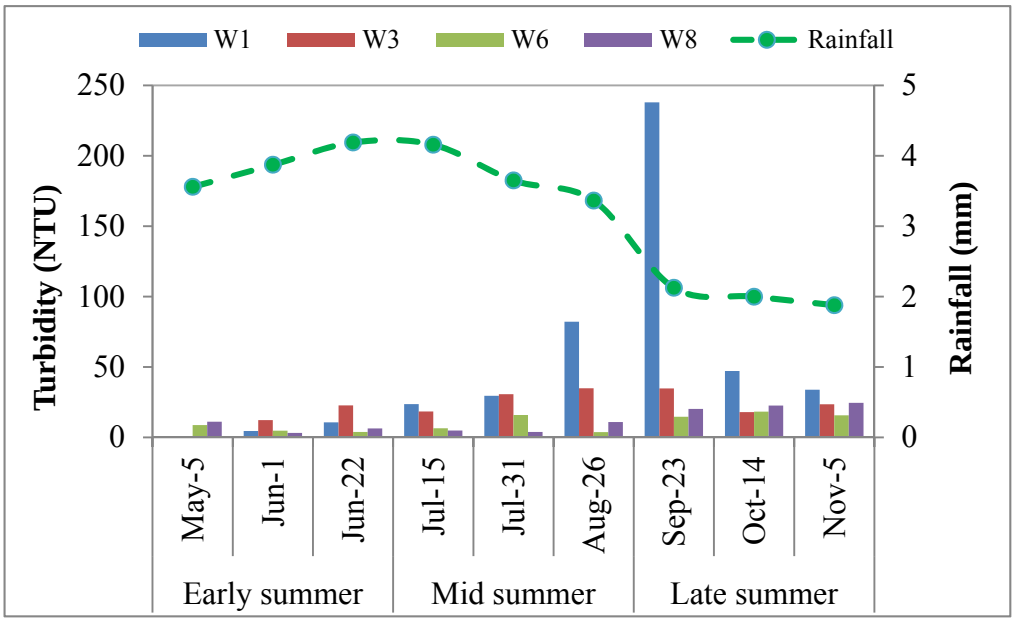


Figure 28: Distribution of turbidity and its relationship with the rainfall at specific sites during the study period

The test results for turbidity showed a minimum value of 2.5 NTU (at site W9 on June 1) and a maximum value of 238 NTU (at site W1 on September 23) with an average of 21.35± 4.14 NTU (Table A1 & B1, Appendix A & B). Large rain events took place from early to mid-summer, causing a high load of suspended solids (mostly algae) to appear in the water body. Because of this, most of the sites showed increasing trend of turbidity during the study period (Figure 28). The turbidity was generally highest at site 1. This site looked murky with hardly any water throughout the sampling period (Figure 29).

Site W1 on July 31 (mat of algae seen)

Site W1 on November 5 (less algae)

Figure 29: View of Site W1 at different sampling periods

The results for TSS showed a minimum value of 1.5 mg/L (at site W8 on June 1) and a maximum value of 426.16 mg/L (site W9 on August 26) with an average of 45.39 ± 9.42 mg/L (Table A1 & B1, Appendix A & B). The high TSS at site W9 was due to the fact that the water level was very low and marked with high suspended sediments during sampling.

The analysis for TSS showed an increasing trend from early summer to mid-summer, subsequently declining toward late summer (Figure 30). A high load of TSS was prominent at W1 during most of the sampling days. The obvious reason for this was an excessive amount of organic load that made the water murky in appearance (Figure 29). Frequent rain events during early summer made a clear impact on most sites by increasing the level of TSS. This made the water turbulent and created favorable

conditions for the growth of algae. Therefore, during mid-summer the mat of algae was clearly visible, which resulted in high TSS as expected (Figure 31).

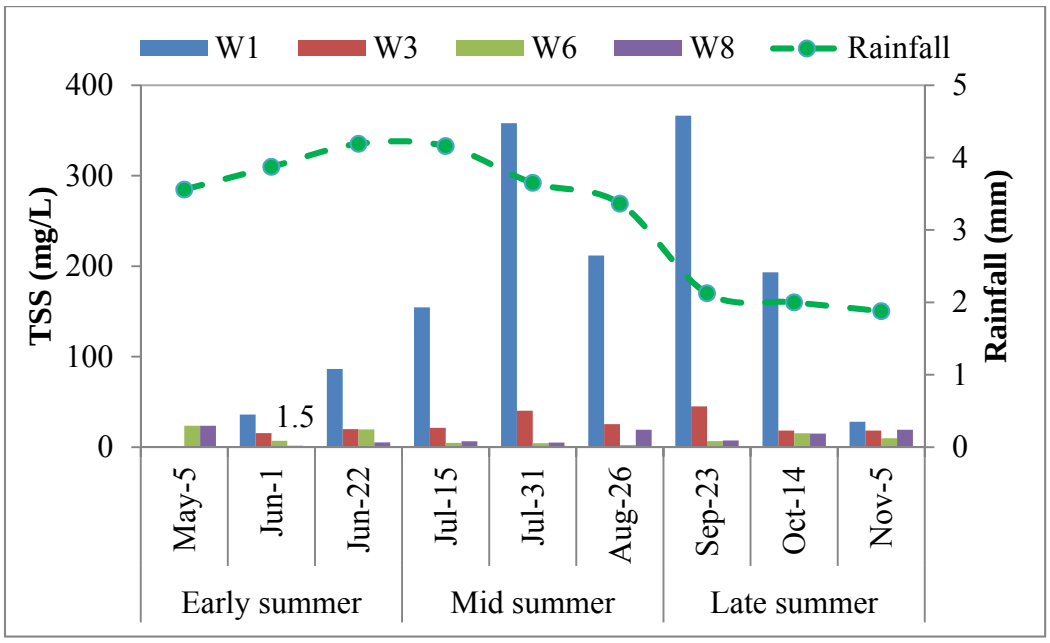


Figure 30: Distribution of TSS and its relationship with the rainfall at specific sites during the study period

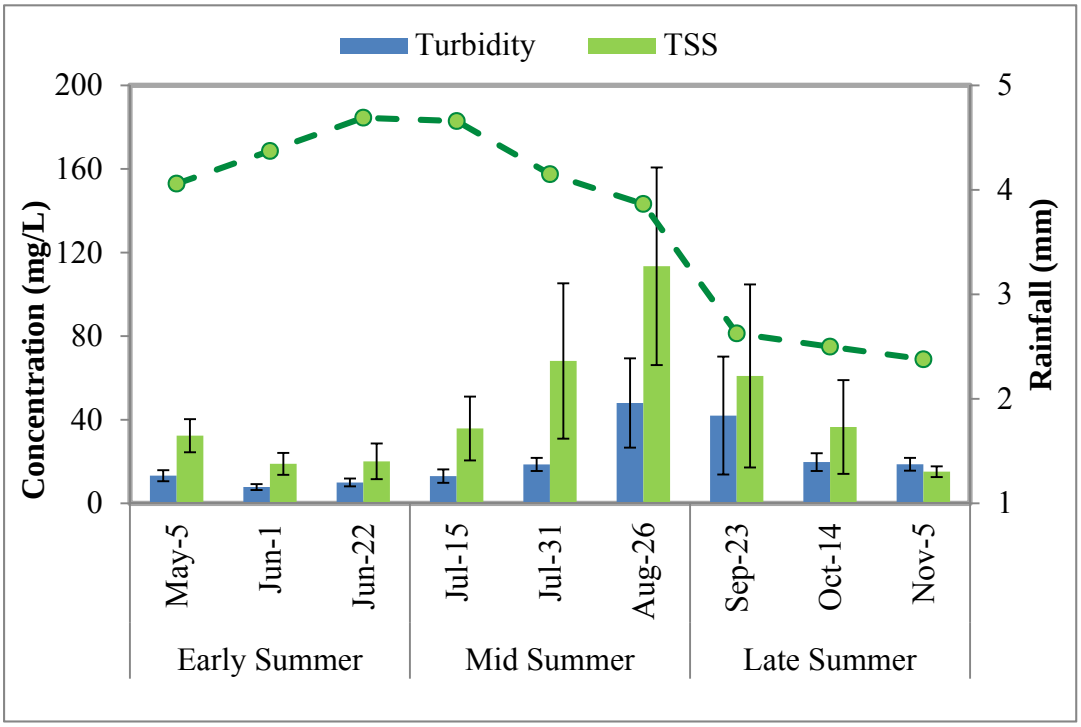


Figure 31: Effect of rainfall on average turbidity and TSS concentration during the study period

Turbidity and TSS are studied as separate parameters. However they are linked to each other as they both measure suspended solids in water. Also, TSS plays a role in increasing the turbidity of water. This study showed a strong correlation (R^2=0.657) between turbidity and TSS in the samples, and was found statistically significant ($p<0.05$) (Figure 32, Table E1 from Appendix E). This correlation also shows that the variability of turbidity to a large degree can be explained by the TSS concentrations.

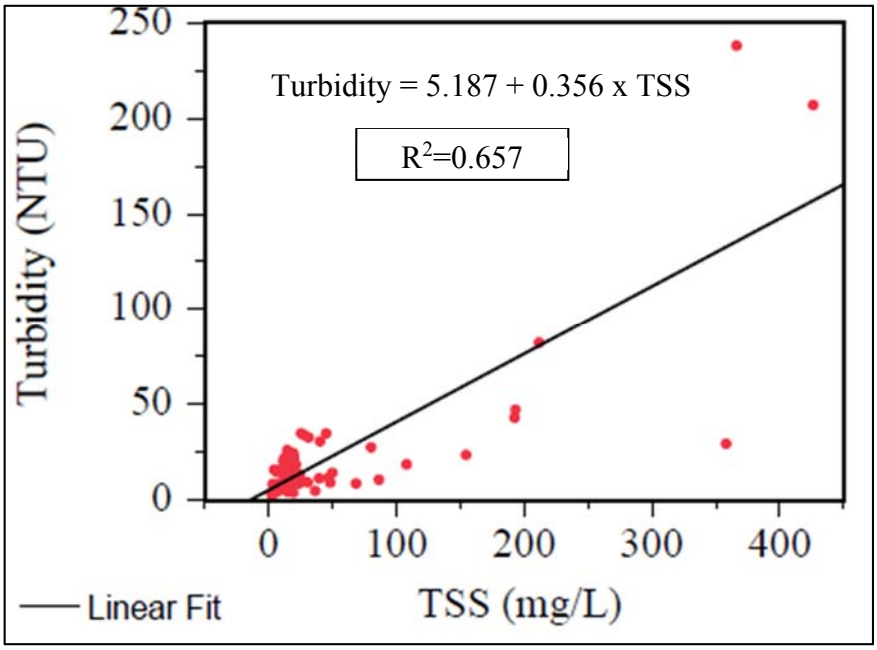


Figure 32: Correlation of turbidity and TSS

Dissolved Oxygen

Dissolved oxygen (DO) is of major concern in monitoring the water quality of any aquatic ecosystem because it supports the metabolism of all aerobic aquatic organisms. The main sources that sustain oxygen level in the water are from the atmosphere and from photosynthesis. Running water with high turbulence has more oxygen concentration compared to still water.

There are many factors that determine the level of dissolved oxygen in water. For example, temperature is a key factor that affects the oxygen level in water. Warmer water holds less oxygen and vice versa. DO levels also vary with altitudes, as high altitudes hold less oxygen than low altitudes. The diffusion process caused by the agitation of the

water surface by winds and waves causes vertical mixing of the water distributing the oxygen within an aquatic ecosystem (USEPA, 1997; USEPA 1991; Ramana et al., 2008). Introduction of oxygen demanding materials, either organic or inorganic, into an aquatic ecosystem causes depletion of the dissolved oxygen in the water. The abundance of aquatic plants and algae influences the level of oxygen. Respiration by aquatic animals, decomposition by microorganisms, and various chemical reactions consume oxygen in water. Because of all these factors, it is possible to have variation in oxygen levels over a 24 hour period or seasonally.

The monitoring of DO is of critical importance when aquatic ecosystems are located in urban areas or adjacent to agricultural fields. Addition of organic materials as wastewater from sewage treatment plants, stormwater from farming or urban streets, and nutrient discharge from agricultural fields can seriously alter the amount of dissolved oxygen in water bodies (USEPA, 1997). Oxygen is partially or completely depleted in the bottom layers since decomposing organic matters accumulated in these layers demand more oxygen (Ramana et al., 2008). Low DO levels in the water may impact aquatic species or impose profound effects on water chemistry, including eutrophication (USEPA, 1991). According to IDNR (2010a), USEPA (1988), Weiner (2000), and Missouri Department of Natural Resources (n.d.), DO criteria have been proposed for surface water which is given in Table 10.

Table 10: *General DO criteria for aquatic organisms*

DO Level in mg/L	Water Quality Status
1-3	Aquatic organism usually dies
3-5	Stress level
5	Minimum level for aquatic organism to live
>8	Healthy level

The summary statistics for DO showed a minimum value of 1.25 mg/L (at site W1 on July 31) and a maximum value of 21.33 mg/L (at site W7 on June 1) (Table B1, Appendix B). The average DO concentration in water was 9.99 ± 0.6 mg/L (Table B1, Appendix B). Figures 33 and 34 both show a spatial and temporal distribution of DO at each site. It should be noted that on May 5, the three initial sites (W1, W2, and W3) were not included because samplings were not initially done for these sites. From both the figures, it is clear that most of the sites in the wetland are well oxygenated. About 11% of the total water samples analyzed were respectively in anoxic (1-3) mg/L and stress (3-5) mg/L levels, and about 79% were in healthy level. The outlet showed an average increase of 57% in DO level during early summer, 83% during mid-summer, and 32% during late summer. This clearly shows that the DO level significantly increased ($p<0.05$, t-test) going from the inlet to the outlet.

Figure 33: Spatial distribution of average DO at each site during the study period

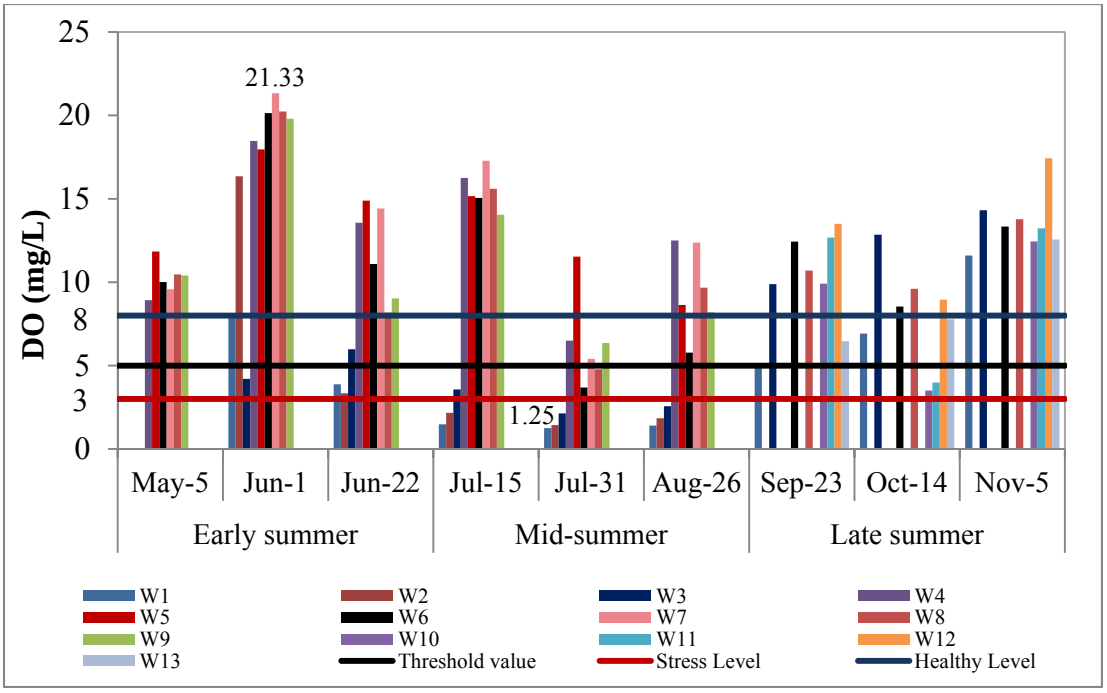


Figure 34: Variations of DO at each site at different sampling periods

The statistically insignificant correlation (R^2=0.0036) and the statistically insignificant ($p>0.05$) relationship between DO and water temperature showed that the concentration of DO was independent of the water temperature (Figure 35, Table E1 from Appendix E). This could mean that the system is capable of maintaining the DO level in spite of rise in water temperature.

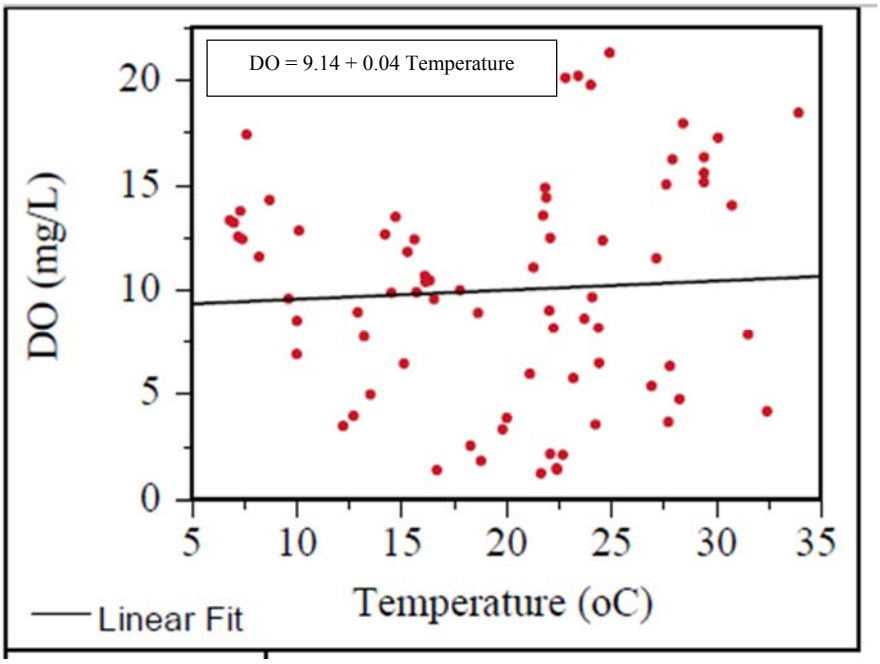


Figure 35: Correlation of DO with surface water temperature

Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) is a measure of the amount of oxygen consumed by microorganisms for the oxidation (i.e., aerobic decomposition) of organic matter (Kadlec & Knight, 1996; USEPA, 1997). In some cases, oxygen is extracted from the water column through the chemical oxidation of inorganic matter for chemical reactions. Some of the factors that determine the rate of consumption of oxygen are pH, temperature, the presence of certain kinds of microorganisms, and types of organic and inorganic matter in the water. High BOD usually means low DO level in the water column, which directly affects the availability of oxygen for use by higher organisms. Therefore, higher aquatic organisms become stressed, suffocated, and could even die because of high BOD in the water. The various sources that deplete the oxygen level and

increase the BOD include, but are not limited to, leaves, woody debris, dead plants and animals, animal manure, wastewater from industries and wastewater treatment plant, and urban stormwater runoff (USEPA, 1997).

In wetlands, organic matter that enters the ecosystem usually contains an approximately 45-50% carbon (C), which is utilized by a wide array of organic C-utilizing microorganisms as a source of energy. These microorganisms convert organic carbon to carbon dioxide by consuming oxygen from the water column, which results in a significant depletion of oxygen (Muzola, 2007). The general BOD criteria can be obtained for various aquatic organisms after reviewing different literatures (Table 11).

Table 11: *General BOD criteria for aquatic organisms*

BOD Level in mg/L	Water Quality Status
1-3	Very clean with little organic waste
3-6	Moderately clean with some organic waste
6-9	Poor with high organic waste and bacteria
>9	Very poor with large amounts of organic waste

In this study, BOD value ranged from a minimum of 0.2 mg/L (at site W2 on July 31) to a maximum of 20.17 mg/L (at site W7 on June 1) with an average value of 5.92 ± 0.48 mg/L (Table A1 & B1, Appendix A & B). During June 1, sites W4 and W7 showed high BOD (greater than 10 mg/L) values until mid-summer, putting these sites in a very poor category (Figure 36 and 37). The results showed that about 32% of the total samples

analyzed (i.e., 75) were in clean (1-3 mg/L), 31% in moderate (3-6 mg/L), 23% in poor (6-9 mg/L), and 15% in very poor categories (>9 mg/L). Although these sites showed high BOD from June 1 through Aug 26, they declined over the rest of the sampling periods (Figure 36). The only plausible reason for high BOD could be the oxygen consumed by bacteria for decomposing the organic matter present in the water. From the figure, it is also clear that the initial three sites (W1, W2, and W3) showed low BOD values in mid-summer. Since the DO concentrations at these sites were not high, it is likely that there was not enough oxygen for the decomposition process to occur. The late summer is typically considered as the fall season, where the leaves start to fall off. In such case, there might be a chance for those leaves to stay in the water for some time and then slowly undergo the decaying process. Therefore, many of the sites showed fairly high BOD values in late summer (Figure 36).

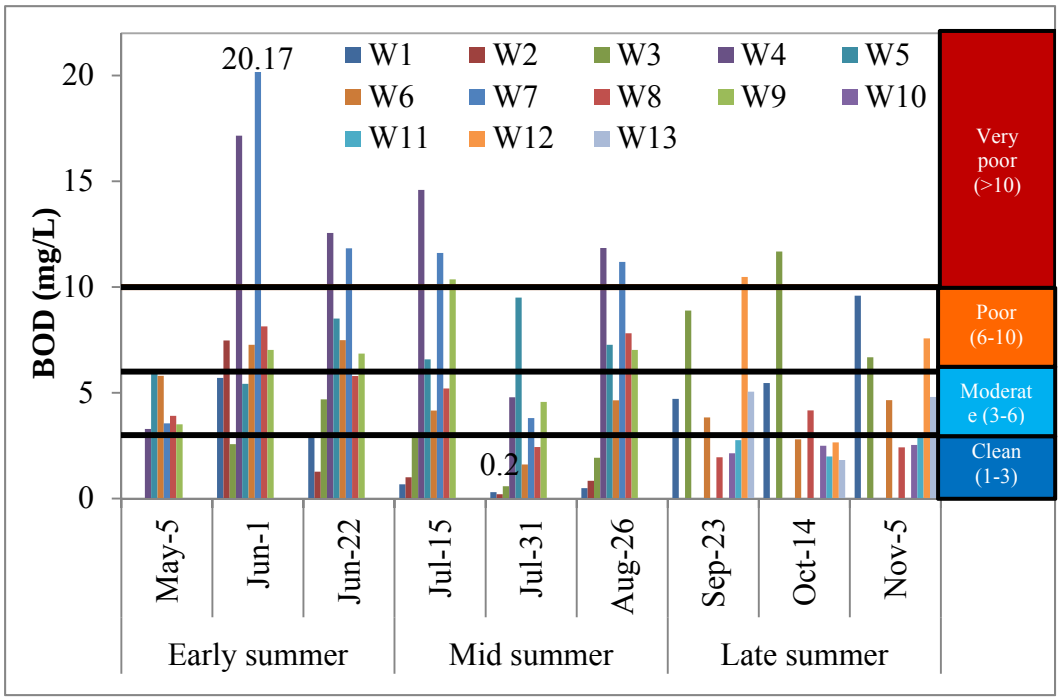


Figure 36: Variations of BOD at different sampling periods

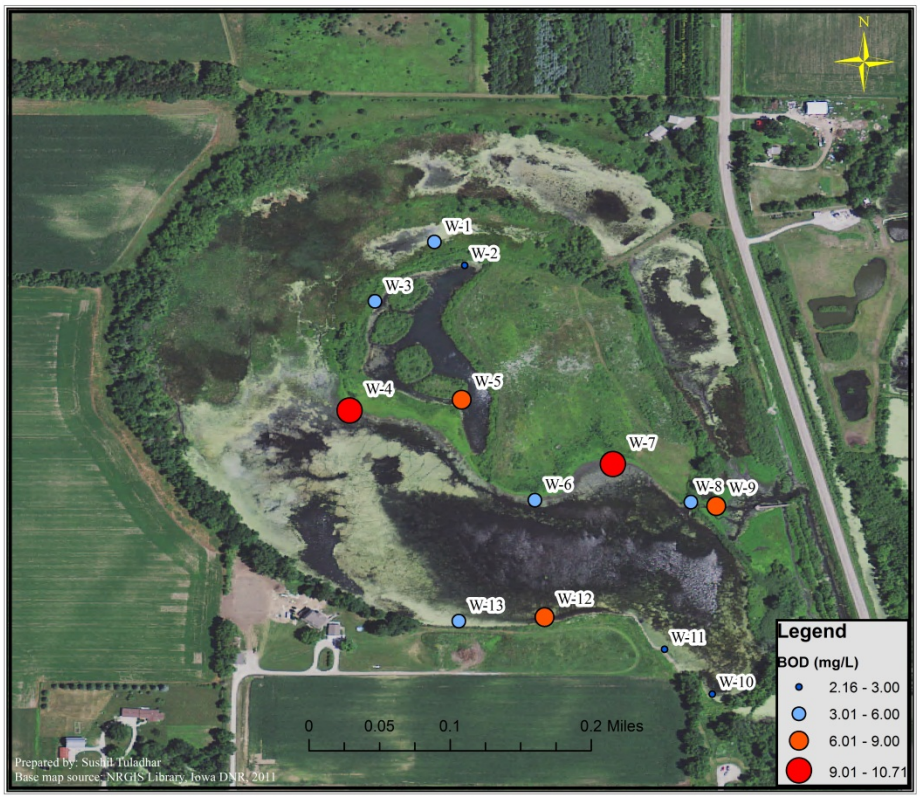


Figure 37: Spatial distribution of average BOD at each site during the study period

Relationship between DO and BOD

It is true that high BOD means rapid depletion of dissolved oxygen (USEPA, 1997). However, in this study the relationship showed no significant relationship between DO and BOD. Figure 38 clearly shows that the sites which had high BOD also had high DO. A moderate positive correlation (R^2=0.568) and statistically significant ($p<0.05$) relationship between DO and BOD were observed during the study period (Figure 39). Although the water samples showed high BOD, it appears that the wetland has the capability to replenish dissolved oxygen rapidly (Weiner, 2000).

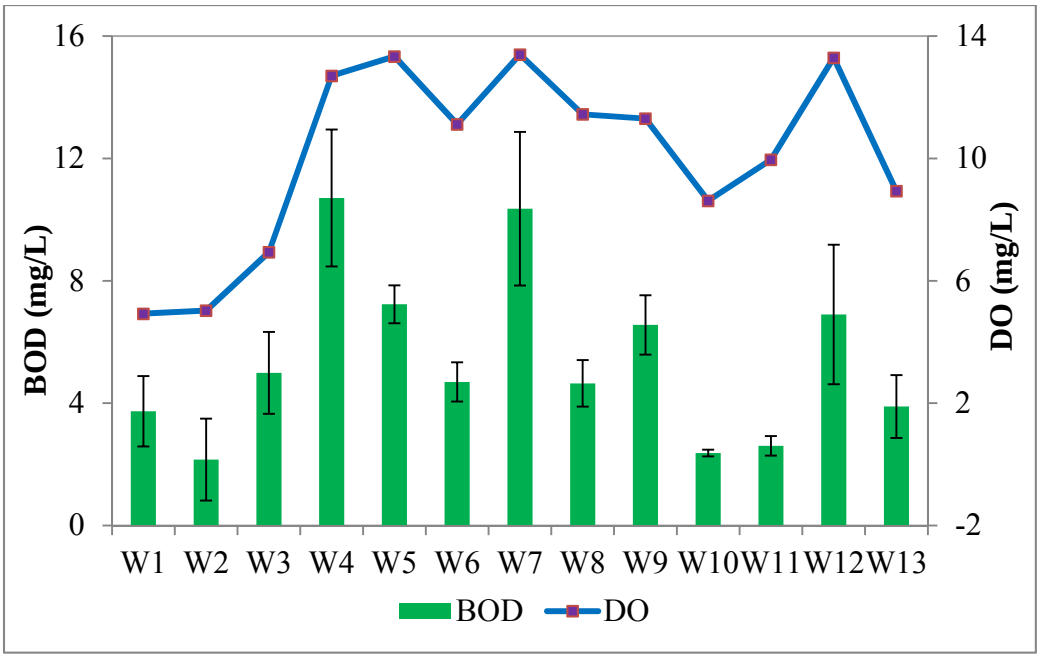


Figure 38: Relationship between average DO and average BOD at each site

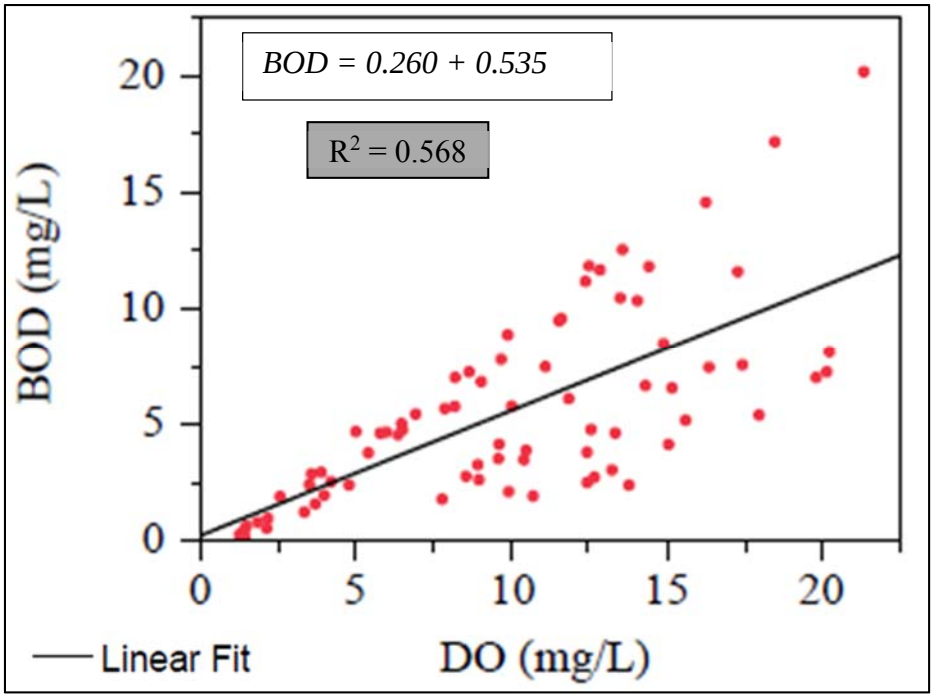


Figure 39: Correlation between DO and BOD

Chemical Water Quality Parameters

Nitrate

Among the various forms of nitrogen, nitrates (NO_3^-) are the most stable and the predominant species utilized by organisms. At low concentrations, nitrates serve as the essential nutrients for plant growth. However, at high concentrations along with other nutrients, they can cause significant water problems, such as eutrophication and algal blooms. Excessive nitrates in water cause hypoxic conditions that can suffocate and kill fish and other aquatic species. All organic compounds containing nitrogen that are being used in the upland areas might cause nitrates to enter the water body at the lowland areas. Once they get into water, they do not adsorb readily onto minerals and soil surfaces (Weiner, 2000). Because of their solubility and mobility, they can raise the background

level of nitrates present in the water. At natural state, the concentration of nitrates is typically below 1 mg/L in surface water, whereas it can be found as high as 30 mg/L in waste water effluents (USEPA, 1997). If the surface or groundwater contains more than 1-2 mg/L of nitrates, then it might indicate agricultural contamination from fertilizers and manure seepage (Weiner, 2000).

In this study, none of the sites showed dissolved nitrates in the water throughout the sampling periods. In natural wetlands, it is possible that nitrate can be used as an electron acceptor during the process of denitrification, where it gets converted to nitrous oxides and nitrogen gas in anoxic conditions (Kadlec & Knight, 1996). This usually occurs when there is high organic matter and less dissolved oxygen, making microorganisms extract oxygen from nitrates to decompose the organic matter. In addition, during the growing season, submerged aquatic plants, algae, and floating plants absorb nutrients from water and sediment. This makes the wetland function more as a "nutrient sink". Therefore, when these plants die (during late fall and early spring), nutrients that were trapped get released into the water column making the wetland function as a "nutrient source". In most cases, nutrients are usually recycled within wetlands. This means, submerged aquatic plants release nutrients into the water column, and on the other hand, algae and floating plants absorb nutrients from the water. When these plants die, they deposit nutrients back on the sediment and settle at the bottom (Miller, 1990).

Chloride

Chloride is one of the major anions widely distributed in nature, and is usually found in the form of sodium, calcium, magnesium, and potassium salts. Naturally chlorides get into the water column from weathering of chloride minerals (Weiner, 2000). Some anthropogenic sources like industrial or municipal wastes, agricultural runoff and road salt release chloride into the water column. Chloride is considered as a major concern in regards to quality of Iowa's surface water because of the high use of road salt during the winter. According to IDNR (2009), the national acute and chronic aquatic life criteria for chloride are 860 mg/L and 230 mg/L respectively.

During the study period, chloride concentration ranged from a minimum value of 7.24 mg/L (W1 on June 22) to a maximum value of 47.56 mg/L (W1 on Nov 5) with an average value of 13.65 ± 0.78 mg/L (Table A1 & B2, Appendix A & B). Out of all 13 sites, the initial 3 sites (W1, W2, and W3) showed comparatively high concentration throughout the sampling periods (Figure 40, 41, 42, and 43). These figures also clearly show that the chloride concentrations are found to be high during mid-summer as compared to other seasons. The sudden increase in rainfall from May onwards and high rainfall recorded during June and July might have played a significant role in having high chloride concentration during mid-summer. While comparing the chloride concentrations between the inlet and the outlet, the result showed less chloride in the outlet than in the inlet (Figure 43). The average percentage reduction was about 44%, and was found to be statistically significant ($p<0.05$, t-test).

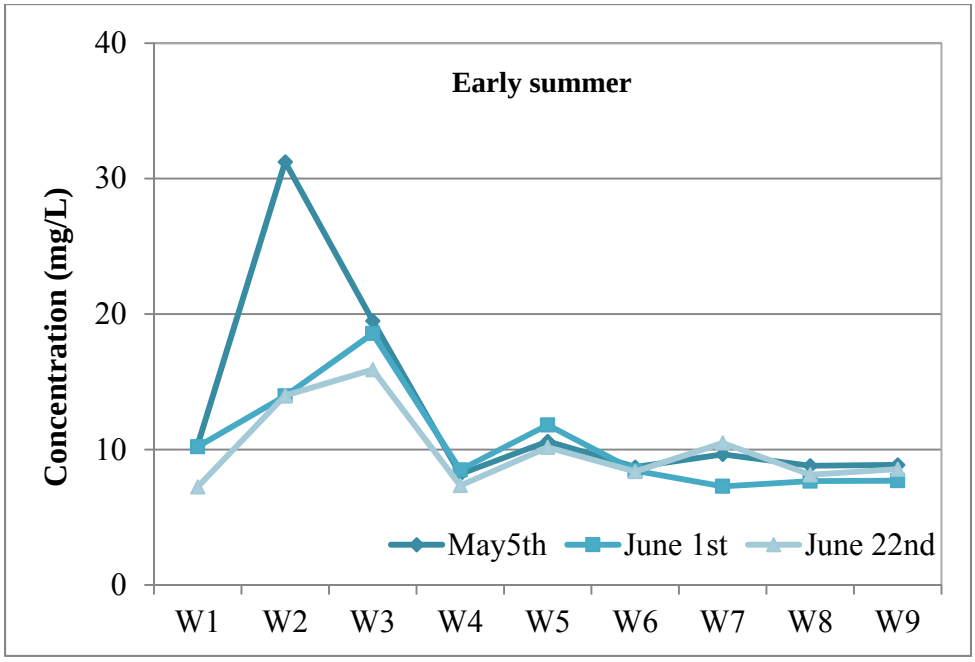


Figure 40: Variations of chloride at each site during early summer

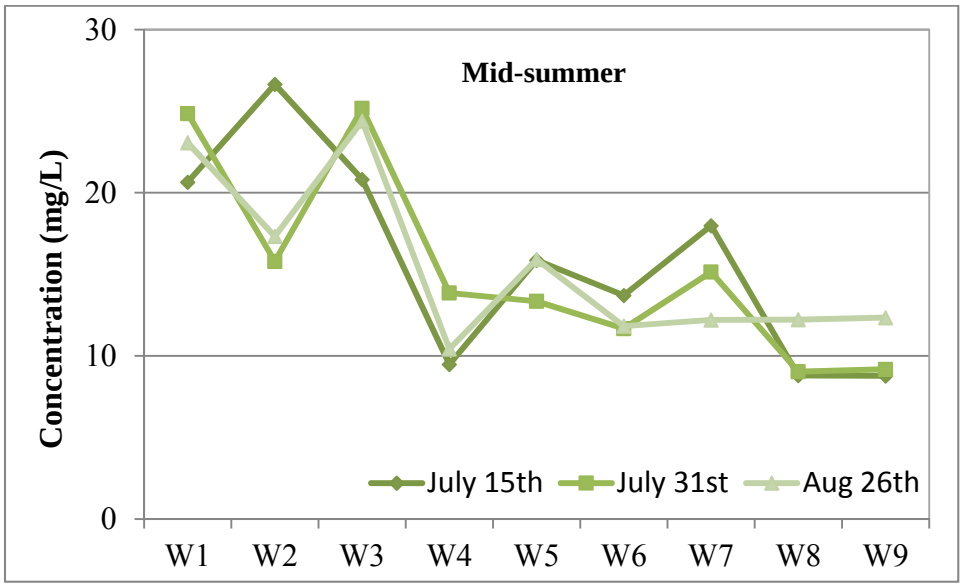


Figure 41: Variations of chloride at each site during mid-summer

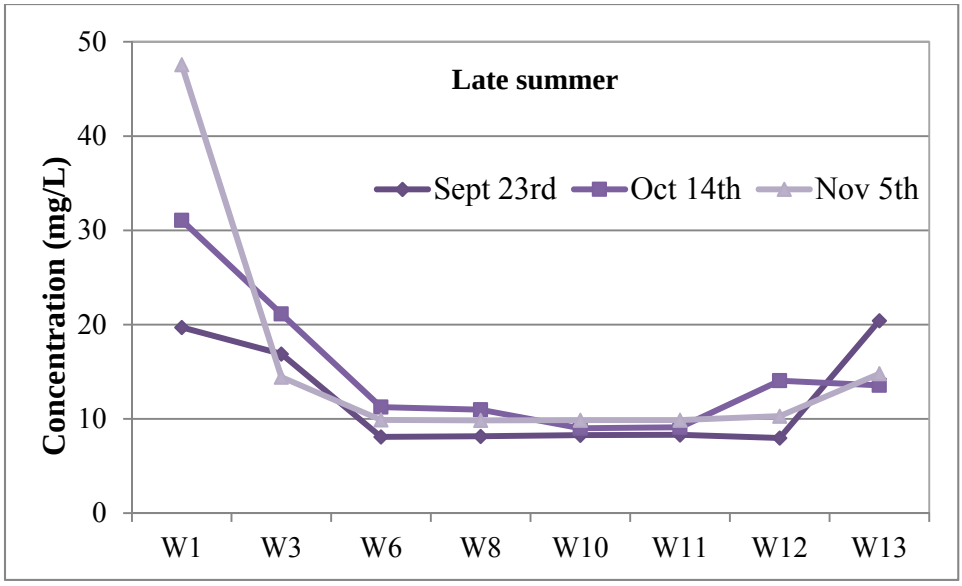


Figure 42: Variations of chloride at each site during late summer

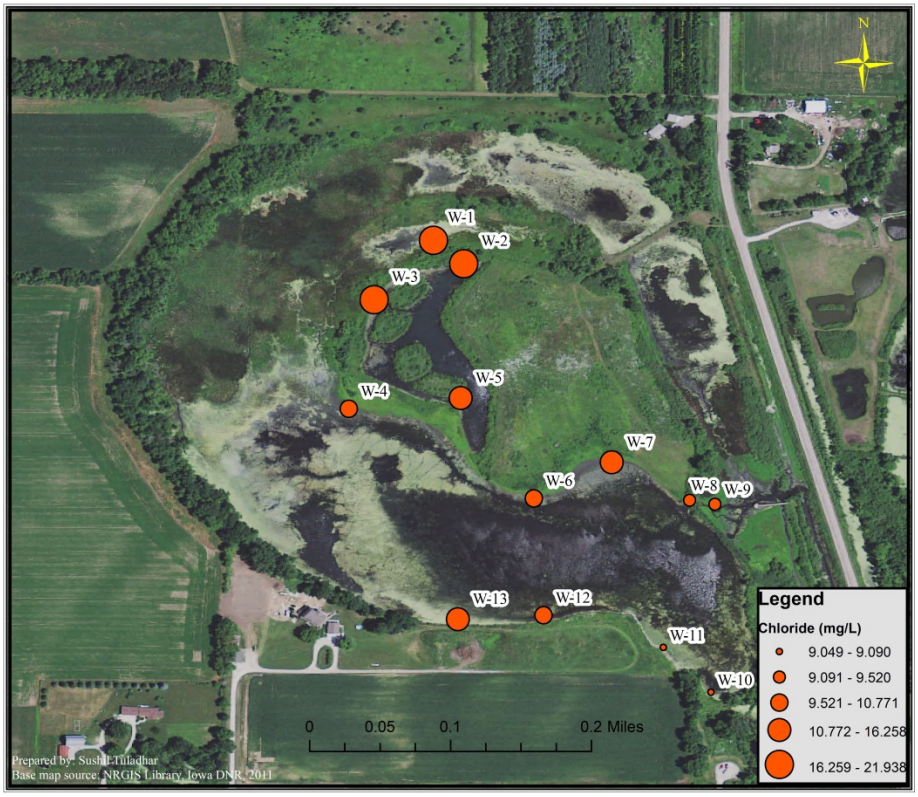


Figure 43: Spatial distribution of average chloride at each site during the study period

Sulfate

Sulfate is also one of the major ions widely distributed in nature. Sulfate, ranging from a few to a several hundred milligrams per liter, is found in natural waters. Naturally, sulfate can reach the water column due to the dissolution of rock containing gypsum ($CaSO_4$). Sulfur-bearing organic materials, when oxidized, can also release sulfates to waters. Anthropogenic sources for sulfate include industrial discharges, industrial fuel combustion, roasting of sulfur-containing ores, acid mine drainage, etc. (Weiner, 2000). Although there are no current federal sulfate criteria for the protection of

freshwater aquatic life, the Iowa water quality standard recommended guideline value is 1,000 mg/L (IDNR, 2009).

In this study, sulfate concentrations ranged from 0.8-38.73 mg/L with an average concentration of 8.78 ± 0.91 mg/L (Table B2, Appendix B). Figure 44, 45, and 46 show temporal variations, and Figure 47 show spatial variations of sulfate concentration at each site throughout the sampling periods. The highest concentration was found at site W1 on November 5. Site W5 showed high concentrations in every sampling months of mid-summer. The remaining sites showed less sulfate concentration in late summer than in the other two seasons. In aquatic systems, scattered gypsum ($CaSO_4$) mineral serves as a natural source for sulfate. In wetlands, under anoxic conditions, bacteria utilize sulfate as an oxygen source that convert sulfate to sulfide (Weiner, 2000). Although the reduction in sulfate was not found statistically significant ($p>0.05$, t-test), after comparing the sulfate reduction between the outlet and the inlet, the result showed an average of 43% reduction at the outlet.

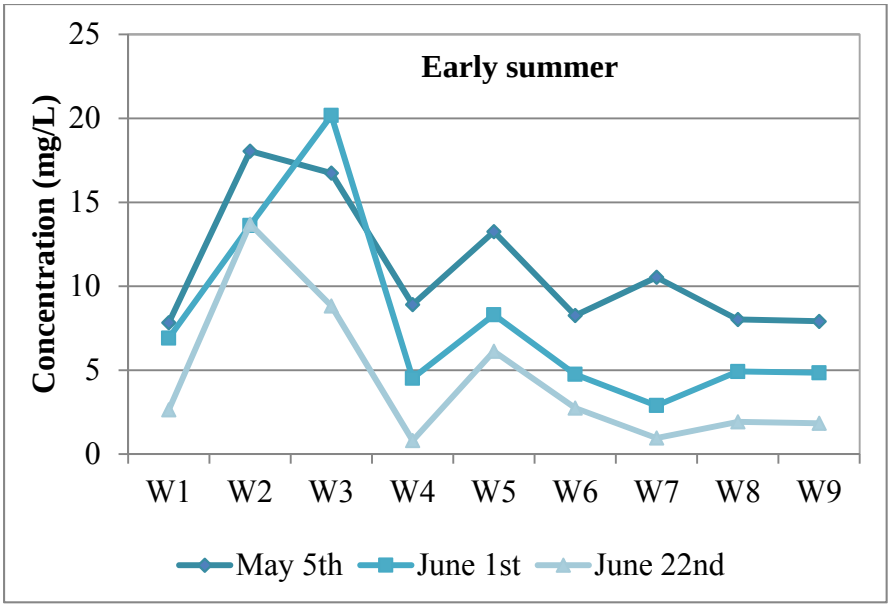


Figure 44: Variations of sulfate concentration at each site during early summer

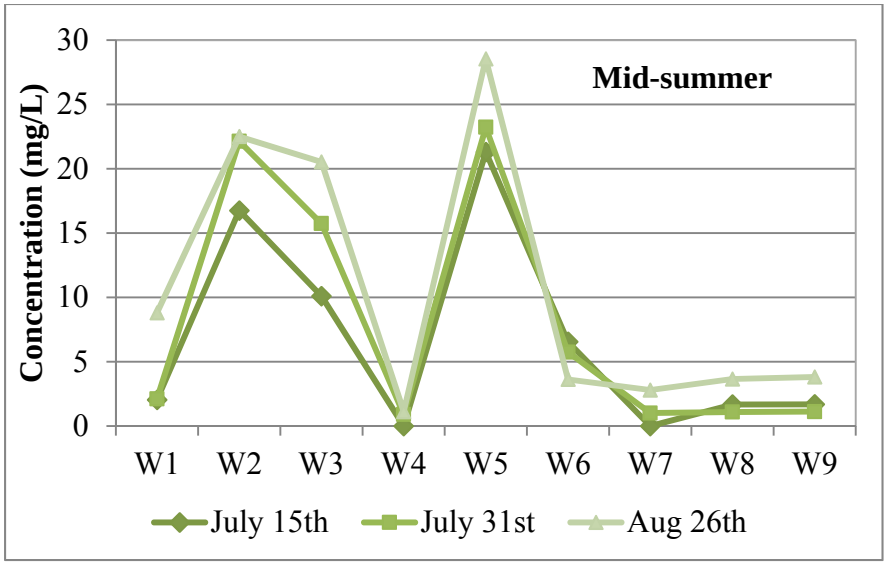


Figure 45: Variations of sulfate concentration at each site during mid-summer

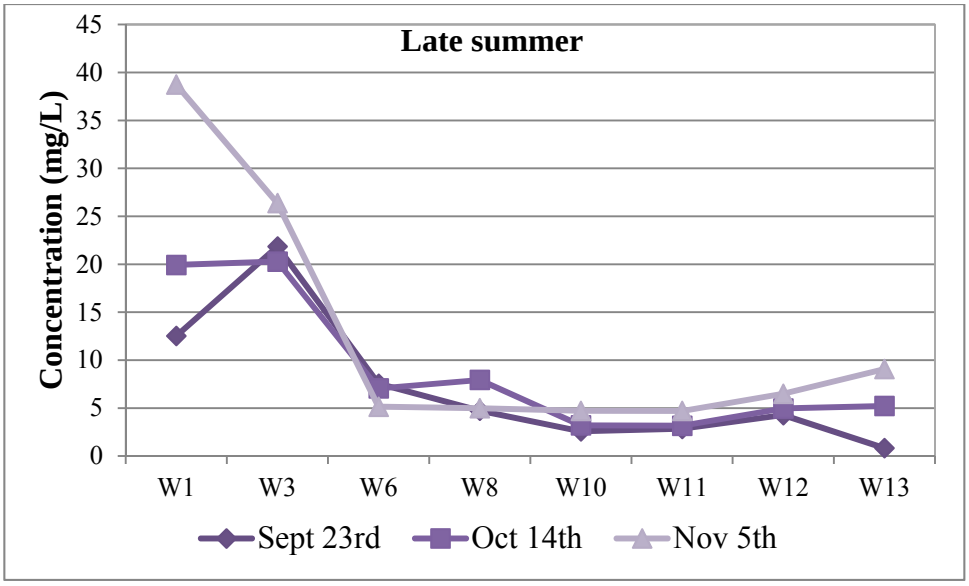


Figure 46: Variations of sulfate concentration at each site during late summer

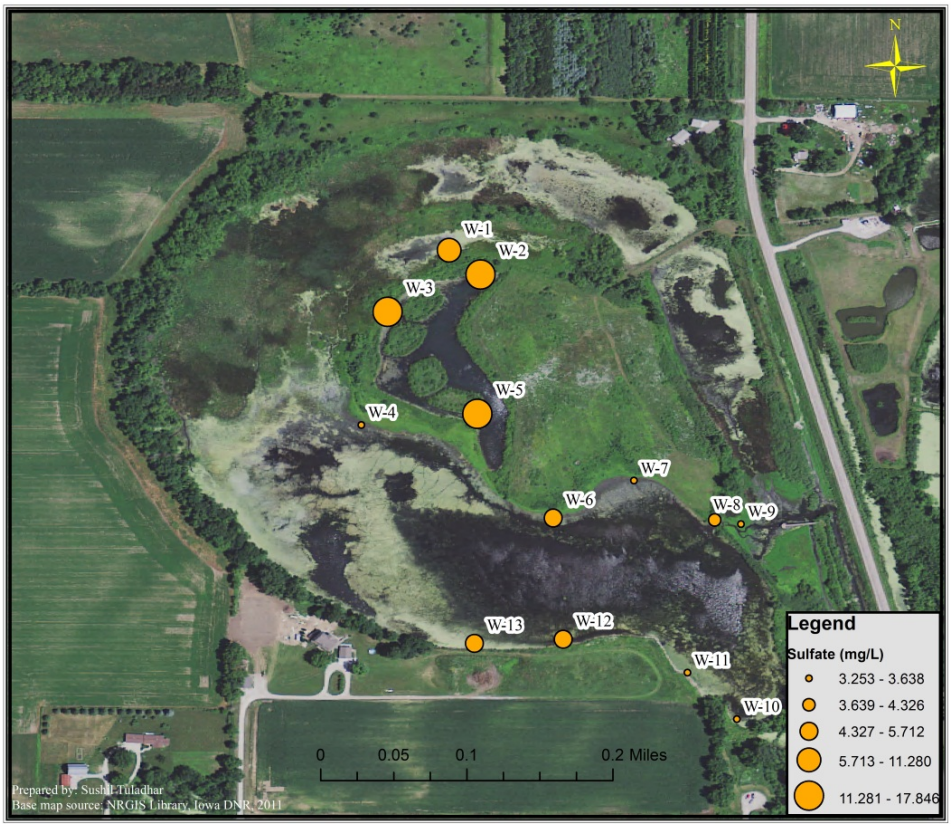


Figure 47: Spatial distributions of average sulfate at each site during the study period

Ammonia

Ammonia is a compound containing nitrogen and hydrogen, and can serve as a nutrient to aquatic plants for their growth. However, it becomes a nuisance in aquatic environment if its concentration gets unacceptably high in surface waters (USEPA, 2009). There are various ways that ammonia can enter into the aquatic environment. Direct sources include the municipal or industrial discharge, and indirect sources include decomposition of plants and animals, nitrogen fixation, and excretion of nitrogenous

wastes from animals (USEPA, 2009). In the wetland, the release of ammonia through the excretion of animal wastes is highly possible because the wetland serves as a migratory habitat for different birds and amphibian species. Some of them include pelicans, ducks, swans, and geese. Ammonia, when released into the water column, can be converted to nitrite (NO_2^-) and nitrate (NO_3^-) by bacteria for plant use.

Ammonia generally exists in two forms in the water; unionized ammonia (NH_3) and ionized ammonia (NH_4^+). The unionized form of ammonia is more toxic than the ionized form to aquatic life, and the toxicity increases as pH and temperature increases (Weiner, 2000). These two forms of ammonia have different characteristics in the aquatic environment. Ionized ammonia is strongly adsorbed on mineral surfaces reducing its mobility, whereas unionized ammonia is weakly adsorbed on mineral surfaces inducing its movement along with water. When suspended sediments carrying ionized ammonia (NH_4^+) reach water having high pH, a portion of it is converted to unionized ammonia (NH_3). Later, this gets desorbed from the sediments and serves as a toxic pollutant to aquatic life forms. Total ammonia ($NH_3 + NH_4^+$) is usually measured in the laboratory, and the determination between ionized and unionized ammonia is calculated from knowledge of the water pH and temperature at the sampling site (Weiner, 2000). According to USEPA (1997), the natural level of ammonia found in the water is typically low, mostly less than 1 mg/L. Ammonia concentrations greater than 0.5 mg/L have significant toxicity to fish populations (Weiner, 2000).

In this study, the concentration of ammonia ranged from 0-2.75 mg/L with an average concentration of 0.19 ± 0.04 mg/L (Table B2, Appendix B).

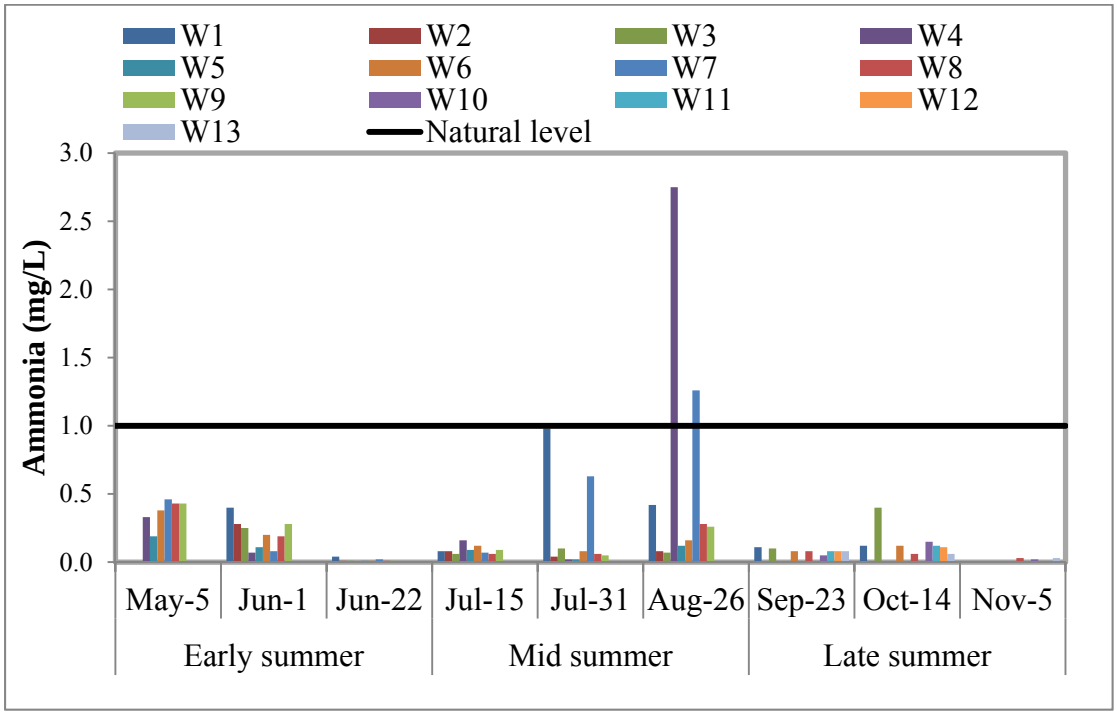


Figure 48: Variations of ammonia at different sampling periods

The concentration of ammonia is significantly high towards the end of mid-summer in most of the sites (Figure 48). The possible reason for this can be attributed to the excreta released from birds (mainly from geese). Since wetlands are considered as temporary migratory waterfowl areas, visits of such birds before regular migration is likely. Although the study did not show any statistically ($p>0.05$) significant differences between the inlet and the outlet, however the results did show an average reduction of about 51% of ammonia in the outlet compared to the inlet.

Phosphorus

Too much or too little phosphorus can have profound effects on the structure of the aquatic ecosystem. For example, low concentrations of phosphorus in the aquatic ecosystem can limit the growth of algae, whereas high phosphorus concentrations can cause high algal blooms leading to eutrophication. When surface inflow along with suspended sediments enters the wetland, there is also a possibility of carrying animal waste, sewage waste, fertilizers, and urban waste from the surrounding areas. This eventually builds up phosphorus in the wetland. Since wetlands effectively flush phosphorus, higher concentrations may not be a concern. However, too much phosphorus coming from the inflow may saturate the soil. In such case, wetlands can be the source rather than sink for the phosphorus. Unlike nitrogen, phosphorus does not easily escape from the wetland.

Water. Figure 49 shows the distribution of phosphorus at each site from May through November. The X-axis represents the sites from W1-W9 for each month from May through August and sites W1, W3, W6, W8, W10, W11, W12, & W13 from September through November. The analysis of phosphorus in the water samples showed various ranges of concentration. The results showed a minimum and a maximum concentration of 97.14 µg P/L and 1712.86 µg P/L, respectively with an average concentration of 418.13 ± 40.04 µg P/L (Table B2, Appendix B). According to the summer 2003 study done by Schwemm (2005) on the Beaver Valley Wetland, the distribution of phosphorus in the water column ranged from a minimum of 100 µg P/L to a maximum of 2000 µg P/L. Most of the sites showed a range of 600 to1850 µg P/L

during June, and it ranged from 800 to 1750 µg P/L during July. The similar ranges of concentrations were also observed in the current study (Figure 49 and 50). Most of the sites, mainly the inlet areas, showed significantly higher concentration than in the other sites. The concentrations were found to be relatively high from June 22 till August 26. Even though the rainfall picked up from May onwards, this was not enough to flush the suspended sediments in the wetland. Therefore, steady dryness and increase in TSS during these months might have played a significant role in the increase of phosphorus concentrations.

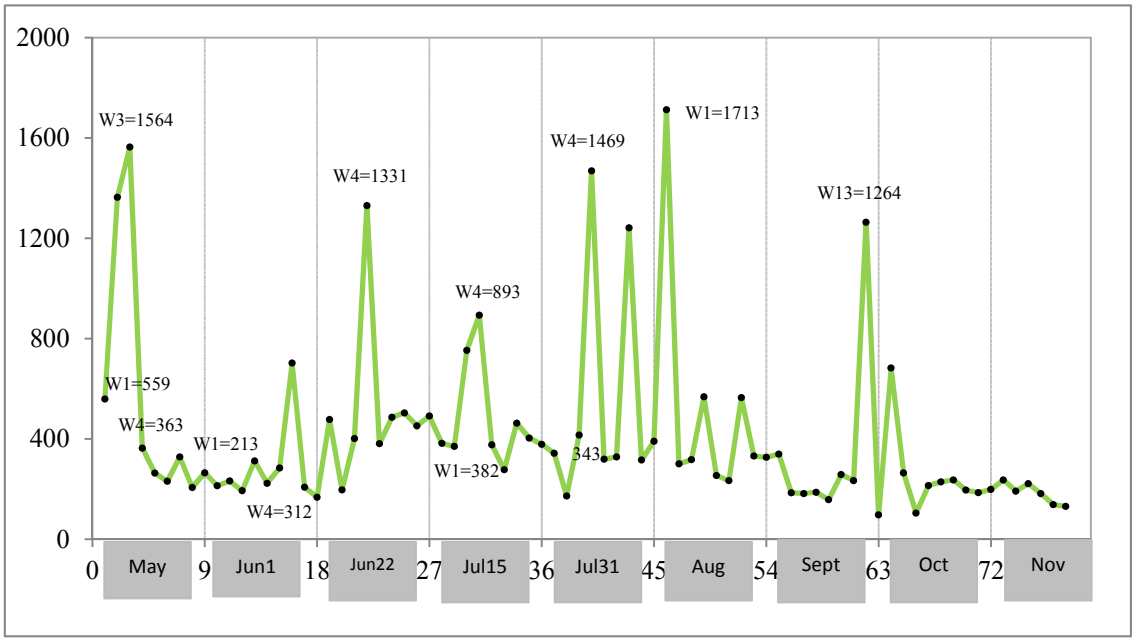


Figure 49: Distribution of phosphorus in µg P/L from May through November

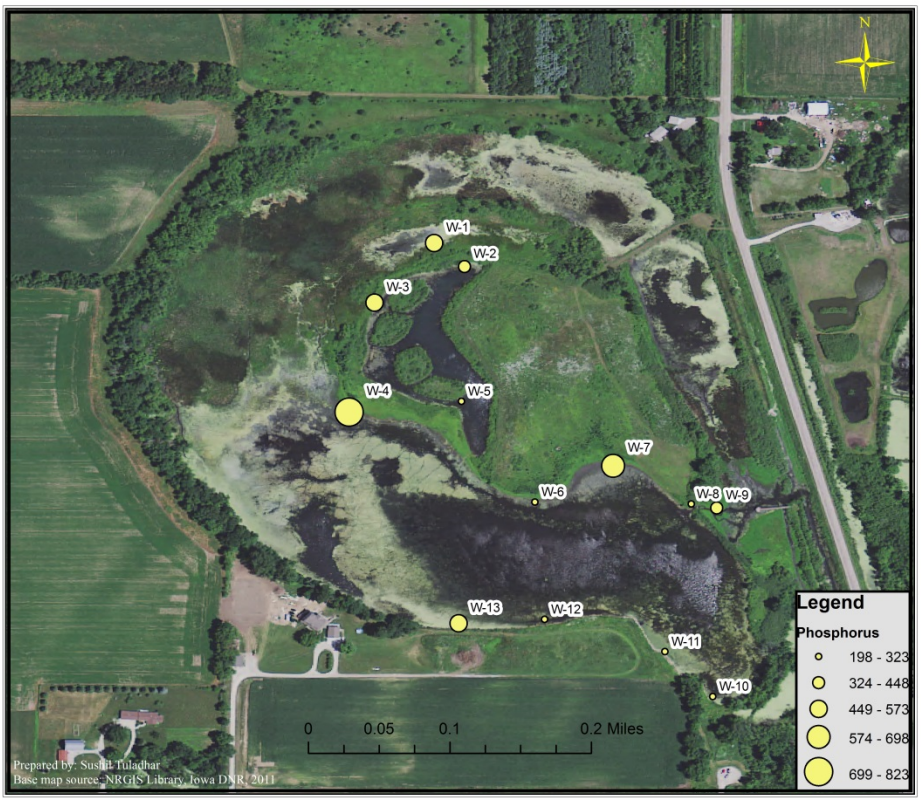


Figure 50: Spatial distributions of phosphorus (µg P/L) at each site during the study period

The phosphorus concentration for most of the sites (especially W1 and W4) peaked during mid-summer (Figure 49). The concentrations started to decline from late summer onwards. The average phosphorus concentrations in W1 during early summer, mid-summer and late summer were 416.44 µg P/L, 812.51 µg P/L and 207.35 µg P/L respectively. Likewise, the average phosphorus concentrations in W4 during early summer and mid-summer were 668.78 µg P/L and 976.56 µg P/L respectively. This clearly shows that the phosphorus concentrations were significantly higher ($p<0.05$, ANOVA) during mid-summer than the other two seasons.

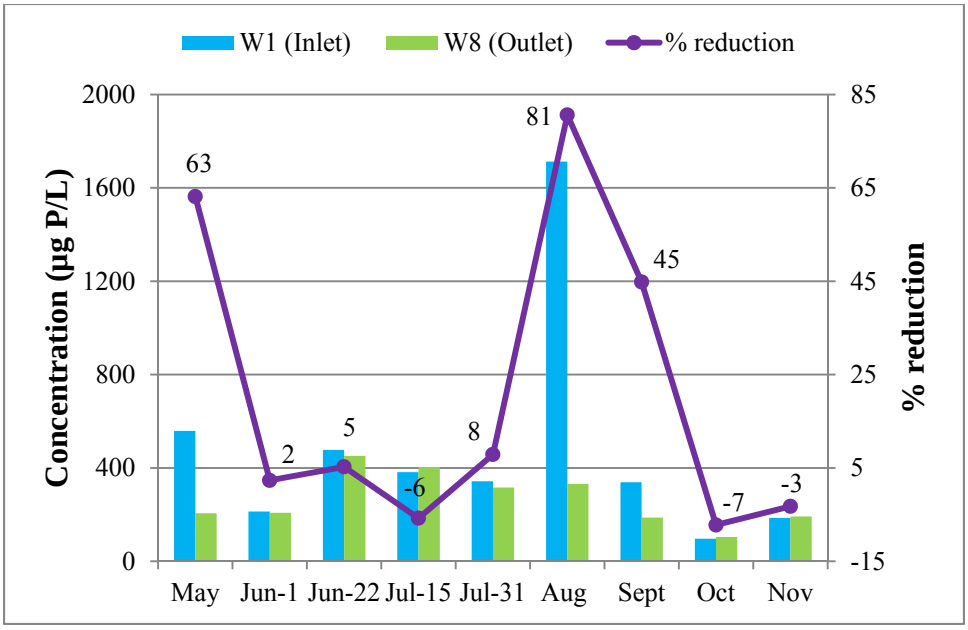


Figure 51: Comparison of phosphorus in the inlet and the outlet sites

The phosphorus concentration was generally higher in the inlet areas than in the outlet areas over most of the sampling periods, as shown by the percentage reduction of phosphorus concentrations between the inlet and outlet sites (Figure 51). Most importantly, the percentage reduction was observed from high to moderate in August, May, and September, respectively. Another important thing to be noted is that the higher the phosphorus concentration in the inlet, the higher the rate of reduction. This clearly explains that the wetland has been effectively removing the phosphorus from the water column.

Sediment. After analyzing the phosphorus content in soils and sediments from different sites, the results showed a minimum of 91.46 µg P/g dry weight to a maximum

of 794.02 µg P/g dry weight with an average concentration of 314.44 ± 29.5 µg P/g dry weight (Table B2 & C1, Appendix B & C).

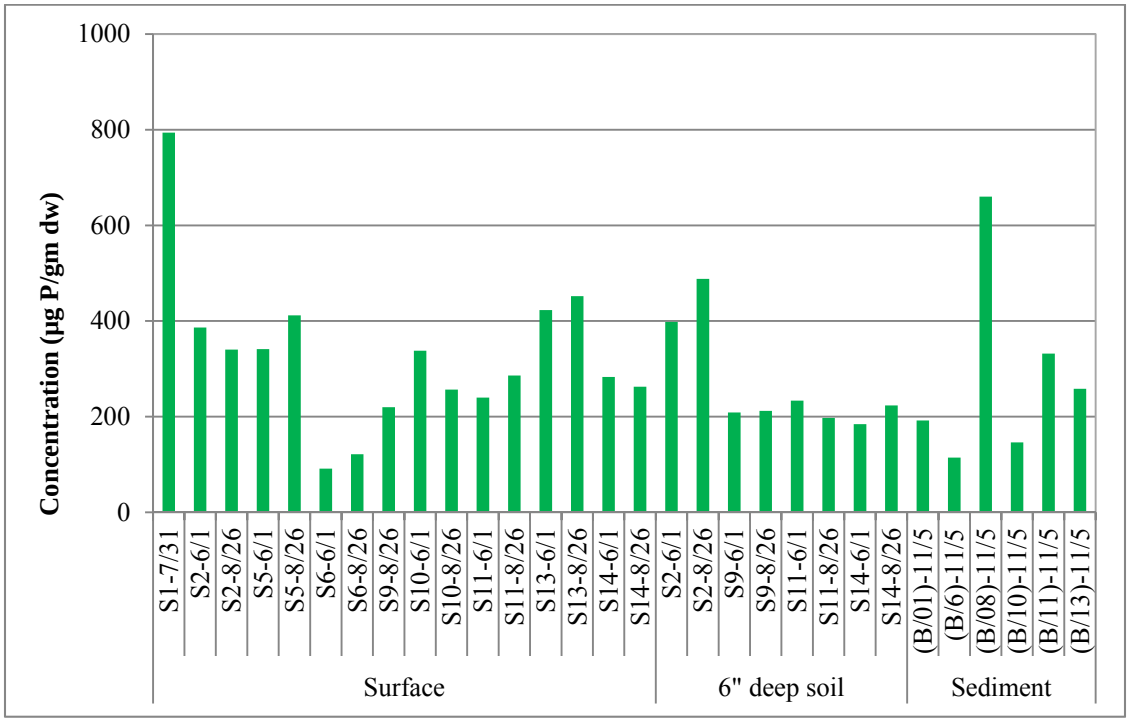


Figure 52: Distribution of phosphorus in sediments at selected sites during the study period

Figure 52 shows the distribution of phosphorus at specific sites in three different sample categories during the study period. It is clear from the figure that the phosphorus concentrations did not vary much among the three categories of sample, and its distribution was also found statistically insignificant ($p>0.05$, ANOVA).

Bacteriological Parameter

Escherichia coli

Escherichia coli (*E. coli*) is the primary fecal coliform bacteria, which is widely used as an indicator organism for determining fecal contamination in the water. When *E. coli* is present in the water, it indicates the presence of enteric pathogens which might affect the health of humans and animals (Weiner, 2000). Currently, it is widely considered as an indicator organism in water quality studies since it provides a good indication of fecal contamination in water. Besides, the cost for *E. coli* testing is small and it is simple to use. It is a specific type of fecal coliform bacteria that occurs in fecal matter from humans and other warm-blooded animals (Weiner, 2000). According to USEPA (1997), *E. coli* is considered the best indicator of human health risk in recreational water bodies. IDNR (2010b) has established a bacterial standard for fresh waters in terms of recreational purpose (especially swimming) at 235 CFU/100 ml (as a one-time sample maximum) and at 126 CFU/100 ml (as a geometric mean).

The presence of *E. coli* in wetlands is common since wetlands serve as a habitat for many birds and other animal species. Also, sediments that runoff from the surroundings to the wetlands can increase the count of *E. coli*. In this study, *E. coli* ranged from 0-400 CFU/100 ml with an average count of 37 ± 7.76 CFU/100 ml (Table B2, Appendix B). Many sites had zero *E. coli* counts during the study period (Figure 53). The number of *E. coli* was found to be high in most of the sites during mid-summer and late summer (Figure 53). Site W9 showed an *E. coli* count of 20 CFU/100 ml on May 5

with no *E. coli* on June 1 and June 22 during early summer. However, the site showed a rise in count with 160 and 400 CFU/100 ml on July 15 and July 31 respectively during mid-summer. Site W8 and W9 showed higher counts than the other sites throughout the sampling periods (Figure 53 and 54). The plausible reason for this can be the increase in rainfall over the early part of summer. Rain washed off surficial materials from the surroundings to the wetland, imposing a pronounced effect on *E. coli* counts. Figure 55 shows the moderate correlation between average *E. coli* and average rainfall, and is statistically significant (R^2=0.506, p=0.0315). Also, the reason for inconsistently high *E. coli* at some of the sites might be due to the presence of birds, such as geese that were seen on the ground as well as in the water during the study.

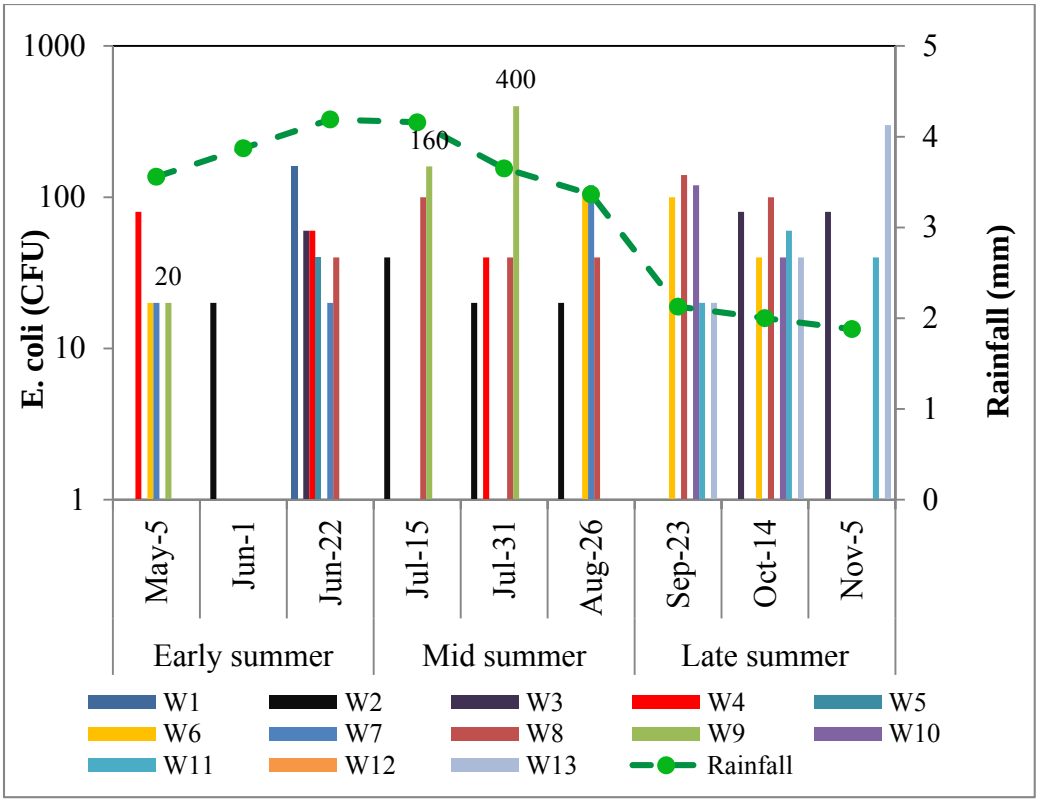


Figure 53: Variations of *E. coli* at different sampling periods

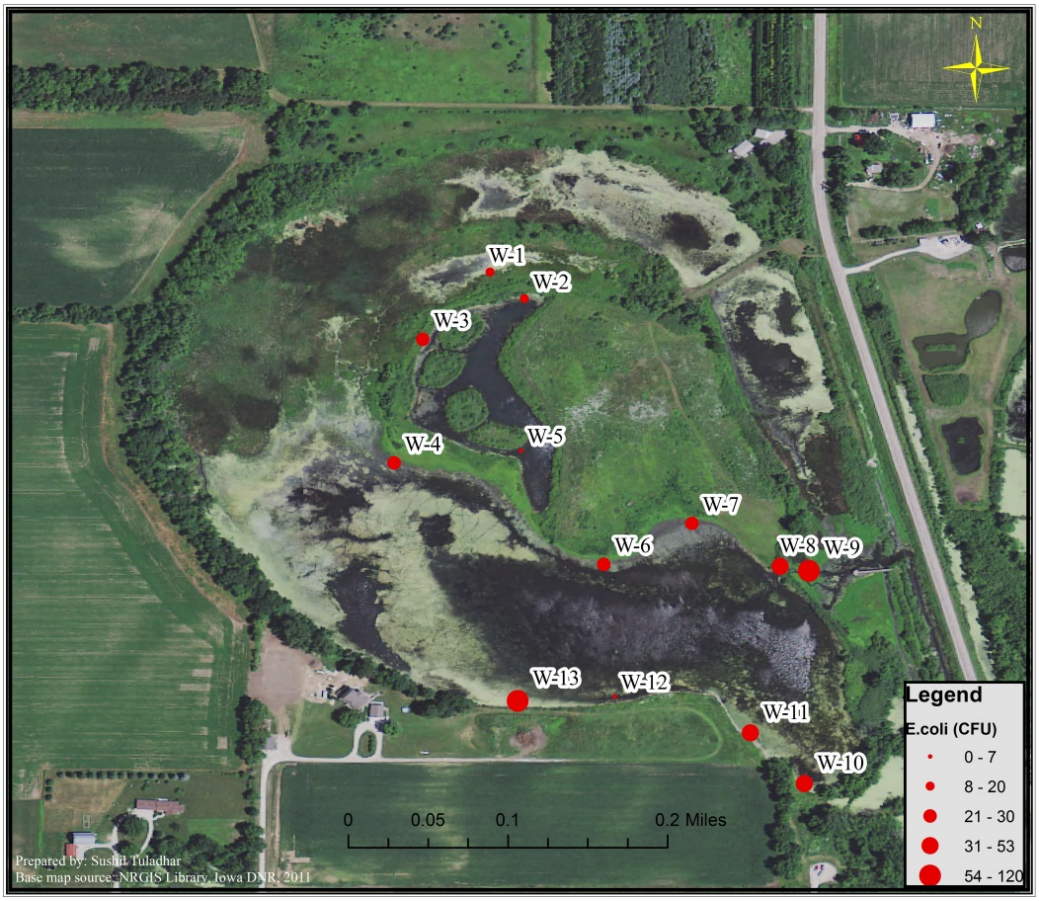


Figure 54: Spatial distributions of average *E. coli* at each site during the study period

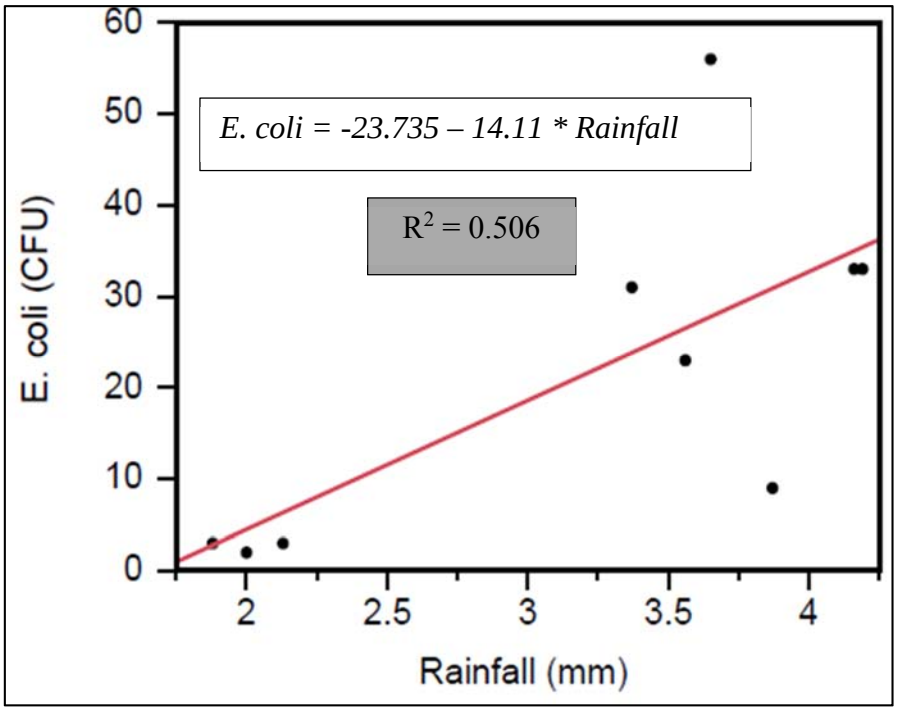


Figure 55: Correlation between average rainfall and *E. coli*

Water Quality Index

The water samples did not show any significant variations in WQI in most of the sites. Out of 75 water samples, 25 samples (33%) were in the range of 50-70 WQI, putting them in the "medium" category. The remaining 50 samples (67%) were in the range of 70-90 WQI, putting them in the "good" category. The result showed a minimum and a maximum WQI of 58 and 89 respectively with an average WQI of 74 ± 0.77. The variations in WQI values were also determined at the specific sites; W1, W3, W6, and W8. This is due to the fact that these sites represent both inlet and outlet areas (W1 & W3 as inlet, W6 & W8 as outlet). The sites were consistently measured throughout the sampling periods (from May through November).

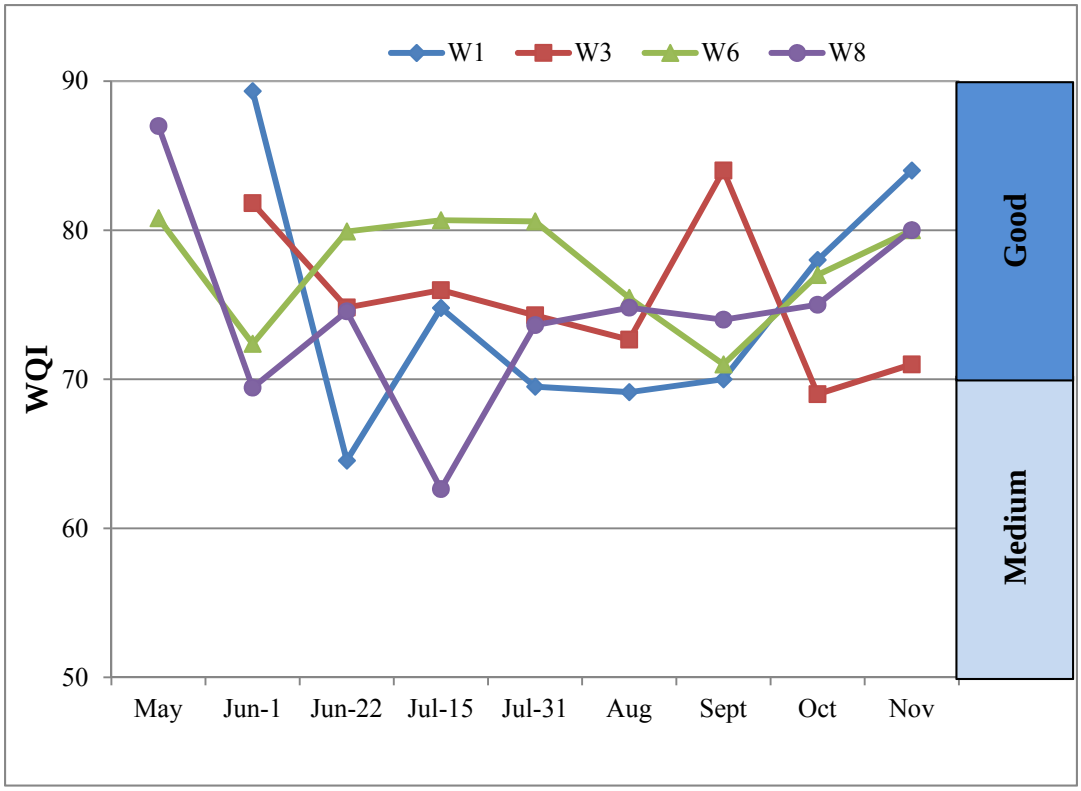


Figure 56: Variations of WQI at selected sites during the study period

All four sites showed WQI in the "medium" and "good" categories (Figure 56). From the figure it is clear that the outlet areas (W6 and W8) had generally higher WQI than the inlet areas (W1 and W3). A sudden drop in WQI from June 1 through July 31 was observed in four sites. This could be attributed to the rainfall, which started to pick up from May onwards and remained high until July 15. Figure 57 shows a slightly decreasing trend in WQI with increasing rainfall even though the relationship is not statistically significant (R^2=0.042, $p>0.05$).

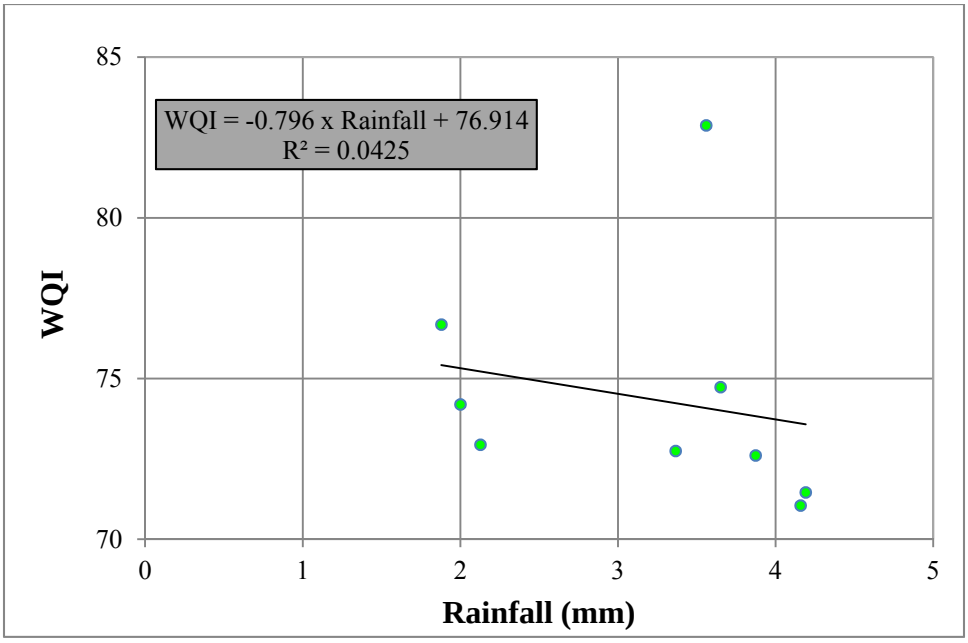


Figure 57: Effect of rainfall on WQI

Heavy Metal Analysis

Trace heavy metals, when present in significant concentrations, may serve as essential micronutrients. But when the concentration of these metals gets high in the aquatic environment through various sources, they might have toxic effects on sensitive organisms (Kadlec & Knight, 1996). In this study, out of 84 samples collected (including soils and sediments), 30 samples were used to study the distribution of heavy metals. The summary statistics for different heavy metals are shown in Table 12.

Table 12: *Summary statistics for different heavy metals*

Units are in mg/kg

Statistics	**Fe**	**Mn**	**As**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Minimum	0.63	0.01	1.08	0.1	8.52	2.69	7.22	6.52	14.47
Maximum	7.97	0.5	11.94	13.34	60.13	19.37	45.94	26.09	82.61
Mean	3.50	0.15	4.57	4.09	32.39	10.59	21.44	15.59	49.77
SEM	0.34	0.02	0.48	0.83	1.98	0.85	1.59	0.80	3.17
Std. Deviation	1.87	0.13	2.66	3.65	10.85	4.68	8.71	4.40	17.36
Median	3.45	0.125	4.01	2.55	31.61	10.77	19.99	15.44	50.07
Variance	3.51	0.01	7.08	13.35	117.72	21.95	75.90	19.43	301.49

Iron (Fe)

Iron serves as an essential metal in the aquatic environment, and when present in significant concentrations it may benefit plants and animals for their nutritional and energy requirements (Kadlec & Knight, 1996). Iron is present in two oxidation states in the aquatic environment: ferrous (Fe^{2+}) and ferric (Fe^{3+}), among which ferrous is highly soluble at desirable pH range and is also dominant in reduced conditions in wetlands and other aquatic environments. Ferric is less soluble at pH >5 and is the dominant ionic form under oxidized conditions (Kadlec & Knight, 1996; Weiner, 2000). Iron enters the aquatic system through the weathering process of pyritic ores containing iron sulfide (FeS_2) and iron bearing minerals. It also comes through many human activities that include mineral processing, coke and coal burning, acid-mine drainage, iron and steel industry wastes, and corrosion of iron and steel (Weiner, 2000). Apparently, iron-bacteria can extract iron from the minerals as an essential nutrient and release them into the water.

The summary statistics presented in Table 12 show that the iron concentrations in this study ranged from 0.63 to 7.97 mg/kg with an average concentration of 3.5 ± 0.34 mg/kg.

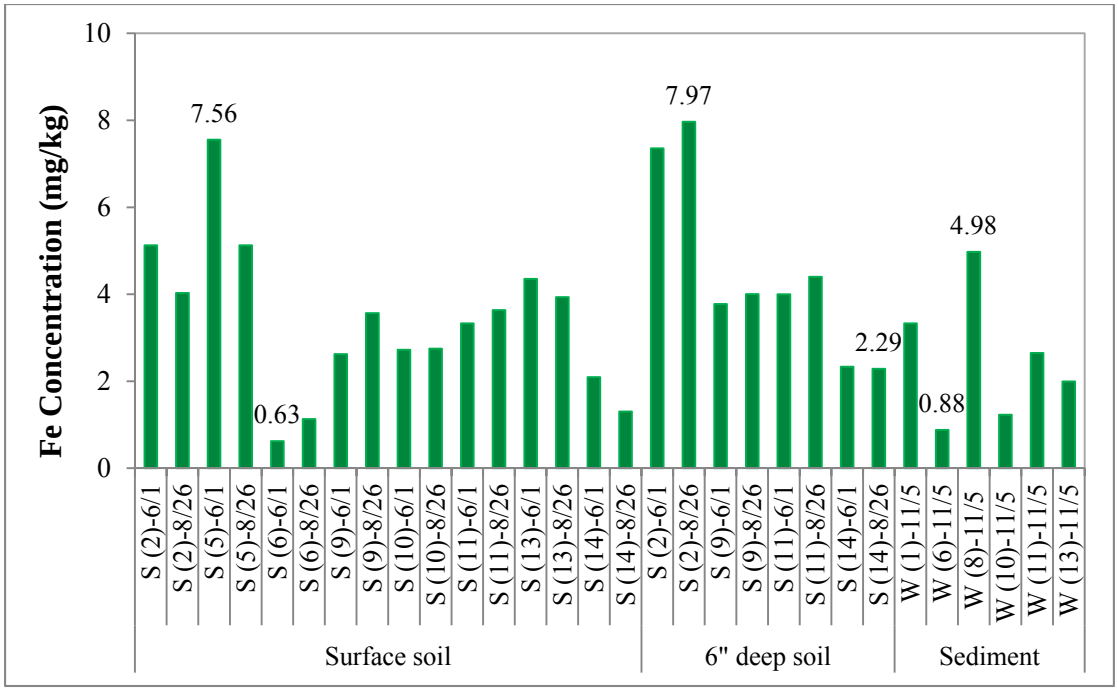


Figure 58: Variations of iron at selected sites during the study period

Figure 58 shows the distribution of iron at selected sites during the study period, and it is clear that iron was found to be relatively high in deeper soils compared to surface samples. The concentration of iron was found to be much less in sediments collected from the wetland.

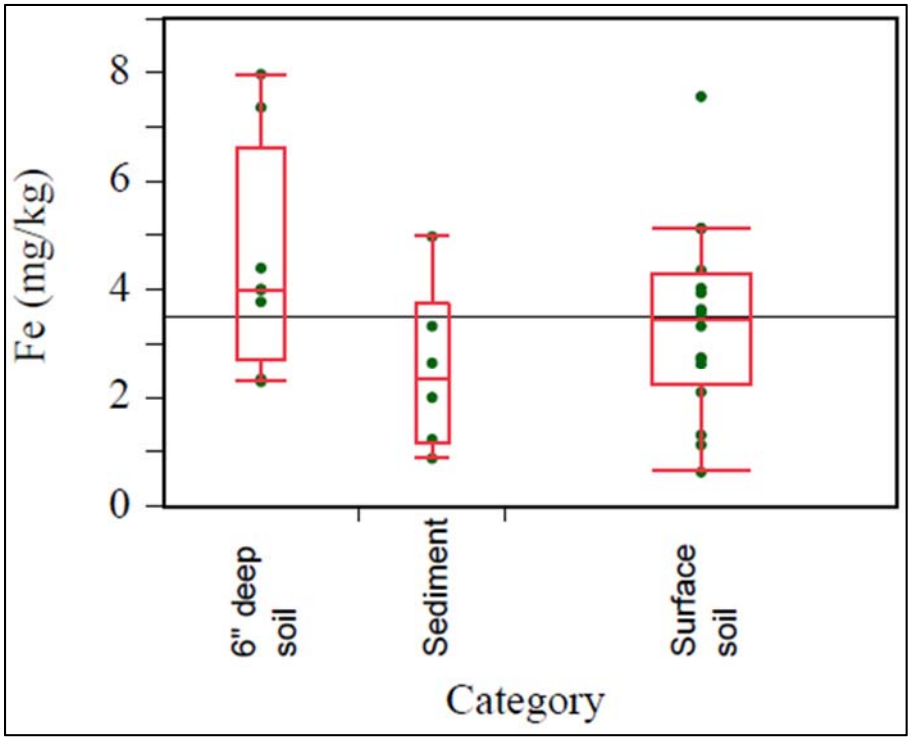


Figure 59: Distributions of iron in three different sample categories

Although the analysis showed an insignificant difference in the distribution of iron in three different soil categories ($p>0.05$, ANOVA) (Figure 59, Table E3 from Appendix E), the iron concentrations were generally lower in the surface soils (0.63-7.56 mg/kg) and sediments (0.88-4.98 mg/kg) than in the 6" deep soils (2.29-7.97 mg/kg) (Table D1, Appendix D).

Manganese (Mn)

Manganese is one of the most abundant and widely distributed metals in the environment. Although it is toxic at elevated concentrations, it serves as an essential element for many plants during photosynthetic processes (Kadlec & Knight, 1996). The

possible sources of manganese to the environment include the steel industry where it is used for manufacturing metal alloys and dry cell batteries, and the chemical industry for making paints, inks, dyes, glass, ceramics, matches, fireworks, and fertilizers. When manganese gets into the atmosphere through such sources, it is also likely that it can be transported back to the soil by atmospheric deposition (Weiner, 2000). Typically its concentration in natural surface waters is < 100 µg/L, and is rarely found in concentrations of 1.0 mg/L (Kadlec & Knight, 1996; Weiner, 2000). Since manganese is found in insoluble forms in the soil, its concentrations are usually low in surface water. Agricultural soils contain an average concentration of manganese of 800 mg/kg dry weight, freshwater wetland soils contain less than 10 mg/kg dry weight, and saltmarsh soils contain up to 400 mg/kg dry weight (Weiner, 2000).

In this study, the concentrations of manganese ranged from 0.01 to 0.5 mg/kg with an average concentration of 0.15 ± 0.02 mg/kg (Table 12). The distributions of manganese in these sample categories showed significantly less concentration than those compared to the concentrations present in freshwater wetland soils (i.e., 10 mg/kg dry weight). The distribution of manganese in different soil categories clearly showed that the 6" deep soil had higher concentration (0.08-0.50 mg/kg) than those found in the surface soil (0.01-0.49 mg/kg) and sediments (0.02-0.07 mg/kg). Sediment samples showed the least manganese concentrations (Figure 60, Table D1 from Appendix D). The one way ANOVA analysis also confirmed that there was statistically significant difference in the distribution of manganese among three categories of soil ($p<0.05$) (Figure 61, Table E3 from Appendix E).

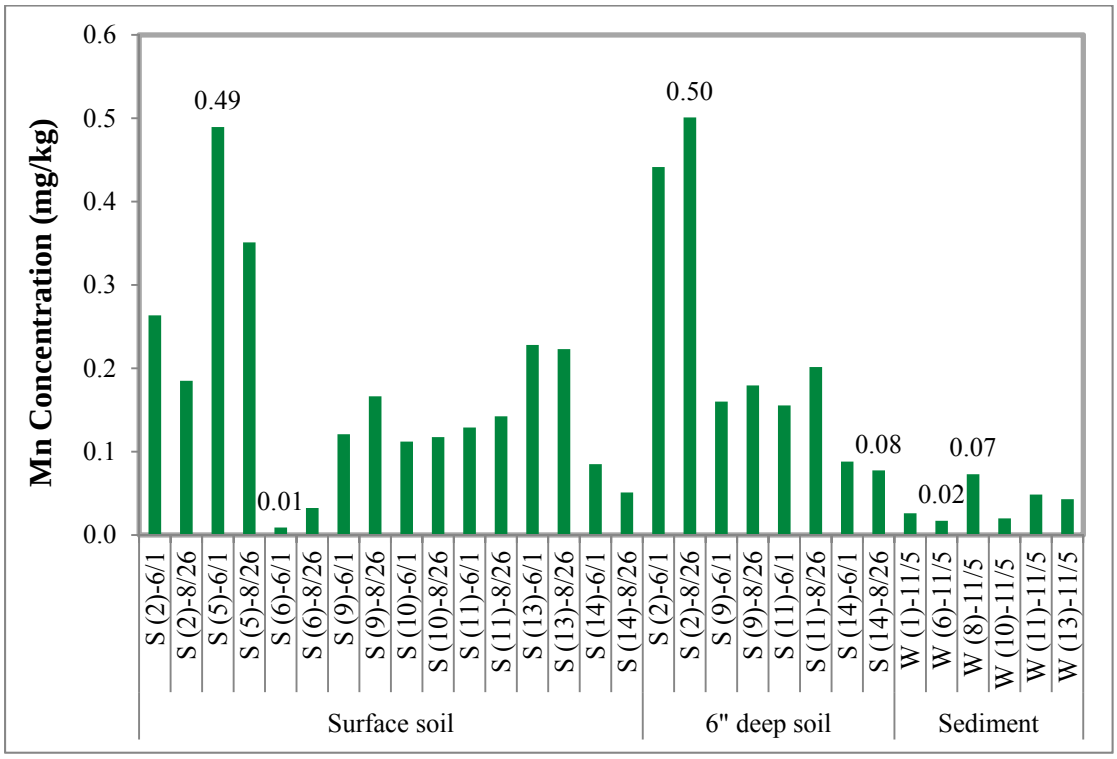


Figure 60: Variations of manganese at selected sites during the study period

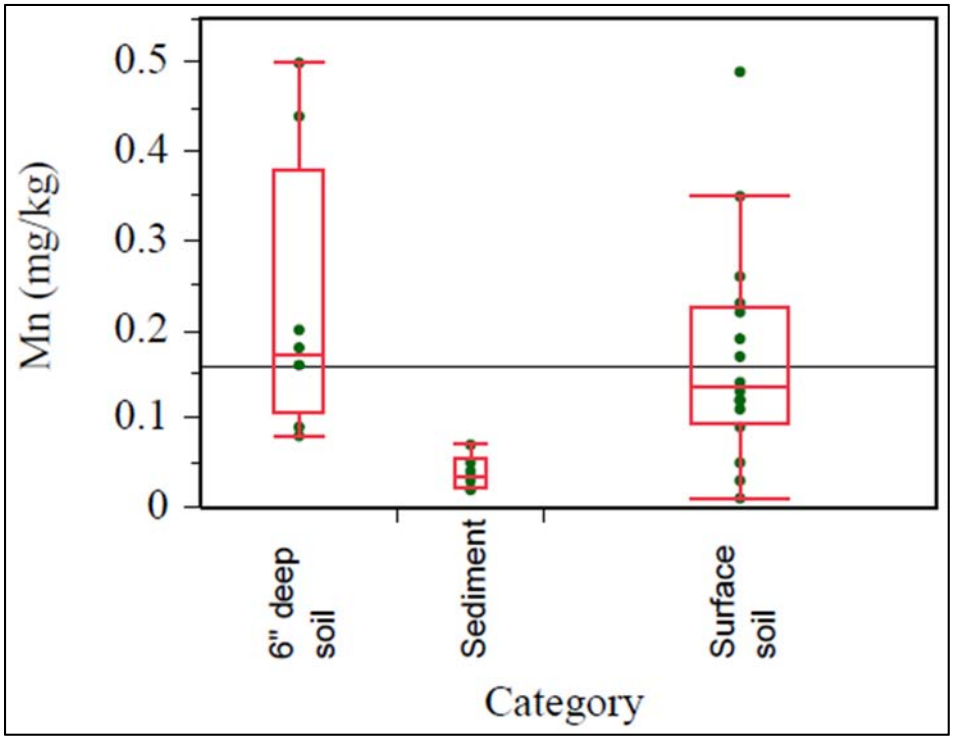


Figure 61: Distributions of manganese in different sample categories

Arsenic (As)

Arsenic behaves both as a metal and a nonmetal, because of which it is also considered as a metalloid. Arsenic is found in two oxidation states as As (III) and As (V), where As (III) is predominant in anoxic environments and As (V) is predominant in oxic soils (Sparks, 2003). Arsenic in the environment could come from natural sources where the element is combined with oxygen, chlorine, and sulfur in minerals. Also, As could come from anthropogenic sources where it is used as wood preservatives, insecticides, and herbicides (Weiner, 2000). The background levels of arsenic in soil range from 1 to 95 mg/kg with a mean concentration of 7 mg/kg for surface soils in the United States (Sparks, 2003; Weiner, 2000).

In this study, the concentration of arsenic ranged from 2.71-11.94 mg/kg in the 6" deep soil, 1.08-11.30 mg/kg in the surface soil and 1.62-3.33 mg/kg in the sediment (Table D1, Appendix D).

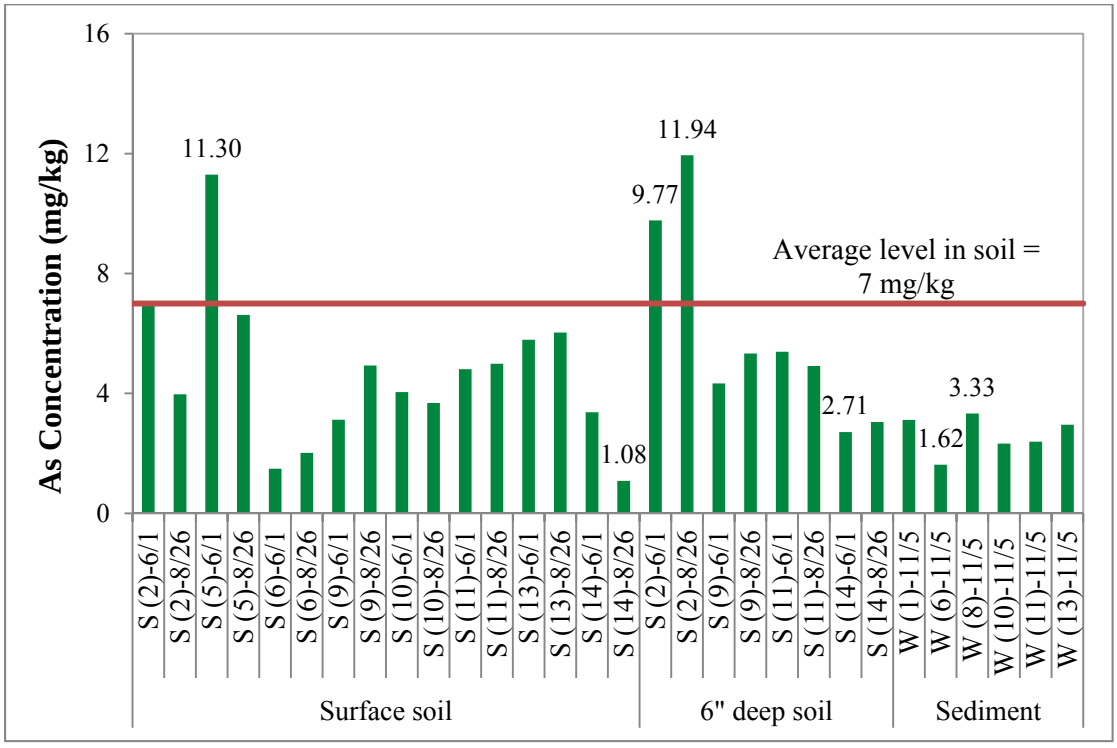


Figure 62: Variations of arsenic at selected sites during the study period

Out of the tested samples, 3 sites, namely S (5)-6/1 (from surface soil), S (2)-6/1 and S (2)-8/26 (from 6" deep soil) exceeded the average concentration (i.e., 7 mg/kg dry weight). These sites showed As concentrations of 11.30 mg/kg, 9.77 mg/kg, and 11.94 mg/kg, respectively (Figure 62). Although two samples from the 6" deep soil showed high arsenic concentrations than the other two soil categories, statistically, it showed moderately insignificant distributions among the sample categories ($p=0.06$) (Figure 63,

Table E3 from Appendix E). Barringer et al. (2001) found an increase of arsenic concentration with depth in some cases because of its high mobility. In highly contaminated soils, the topsoil of wetlands may contain arsenic concentrations up to 260 mg/kg (Kalbitz & Wennrich, 1998).

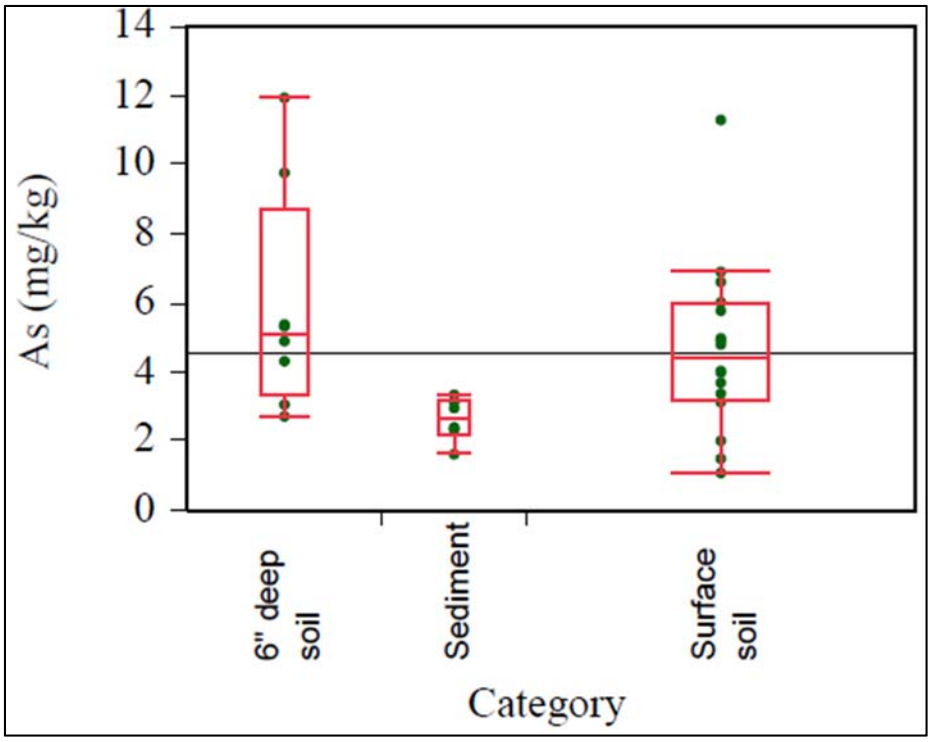


Figure 63: Distributions of arsenic in different sample categories

Cobalt (Co)

Cobalt is an essential trace metal and is relatively rare element in the earth's crust. It usually occurs in association with other metals such as copper, nickel, manganese, and arsenic. Some of the natural sources include volcanic eruptions, natural dust, forest fires,

and other continental and marine biogenic emissions. Anthropogenic sources may include burning of fossil fuel, processing of cobalt-containing alloys, refining and smelting industries, and agricultural pesticides (USEPA, 2005). In the environment, cobalt levels are regulated by pH and they usually occur as divalent cobalt in soils.

In this study, the minimum and maximum concentrations of cobalt were 0.1 and 13.34 mg/kg, respectively with an average concentration of 4.09 ± 0.83 mg/kg (Table 12). In the surface soil, the concentrations of cobalt varied from 0.10-7.85 mg/kg. Similarly, the concentrations in 6" deep soil varied from 1.78-13.34 mg/kg (Table D1, Appendix D). Two soil samples did not have detectable levels of cobalt. Out of 6 sediment samples tested, only 2 samples showed Co levels of 3.45 and 8.71 mg/kg (Figure 64).

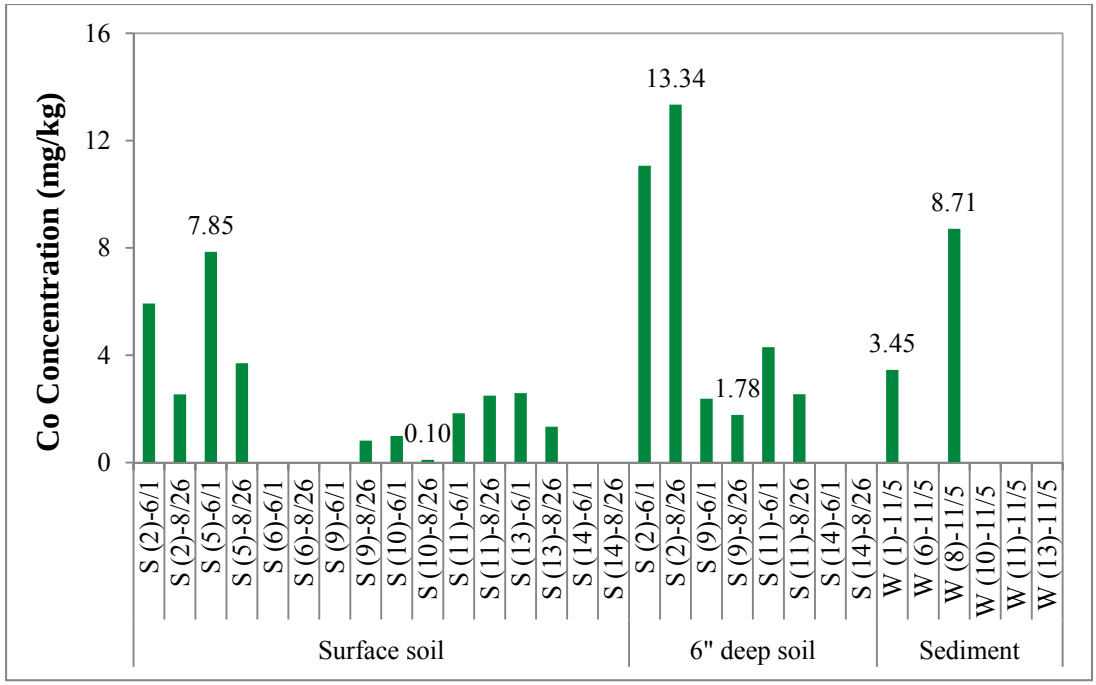


Figure 64: Variations of cobalt at selected sites during the study period

The statistical analysis did not show any significant difference in the distributions of cobalt in three different categories of samples ($p>0.05$, ANOVA). However, the results clearly showed that the concentrations of cobalt in three different categories were in the following order: 6" deep soil > sediment > surface soil (Figure 65, Table E3 from Appendix E).

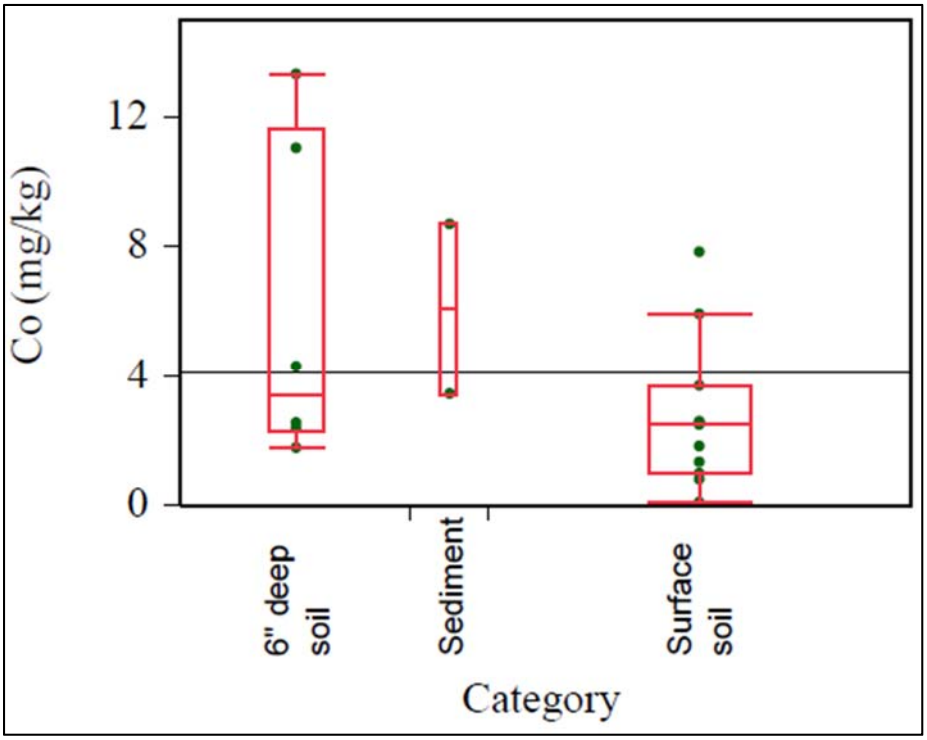


Figure 65: Distributions of cobalt in different sample categories

Chromium (Cr)

Chromium occurs as chrome ion or chromite ($Fe_2Cr_2O_2$) in minerals with an oxidation number +3, whereas it occurs as insoluble chromium oxide (CrO_3) in soils with an oxidation number +6 (Weiner, 2000). Chromium (VI) is relatively unstable under most environmental conditions and gets converted to less toxic chromium (III) in surface waters in the presence of organic matter (Kadlec & Knight, 1996). Some of the natural sources include weathering of rocks and soil. Anthropogenic sources may include metal alloy production, metal plating, cement manufacturing, and incineration of municipal refuse and sewage sludge (Weiner, 2000). In freshwater wetland soils, chromium concentrations are generally below 10 mg/kg dry weight (Kadlec & Knight, 1996),

whereas in the urban soil its concentration ranges from 1-1000 mg/kg (Langner et al., 2011).

This study showed that most of the sites had chromium concentrations above 10 mg/kg. The concentrations of chromium ranged from 8.52-40.63 mg/kg in the surface soil, 22.11-60.13 mg/kg in the sediment, and 24.46-45.33 mg/kg in the 6" deep soil (Figure 66, Table D1 from Appendix D). Although sediment samples had relatively high concentrations, statistically it did not show any significant difference in the distributions of cobalt among three sample categories ($p>0.05$) (Figure 67, Table E3 from Appendix E).

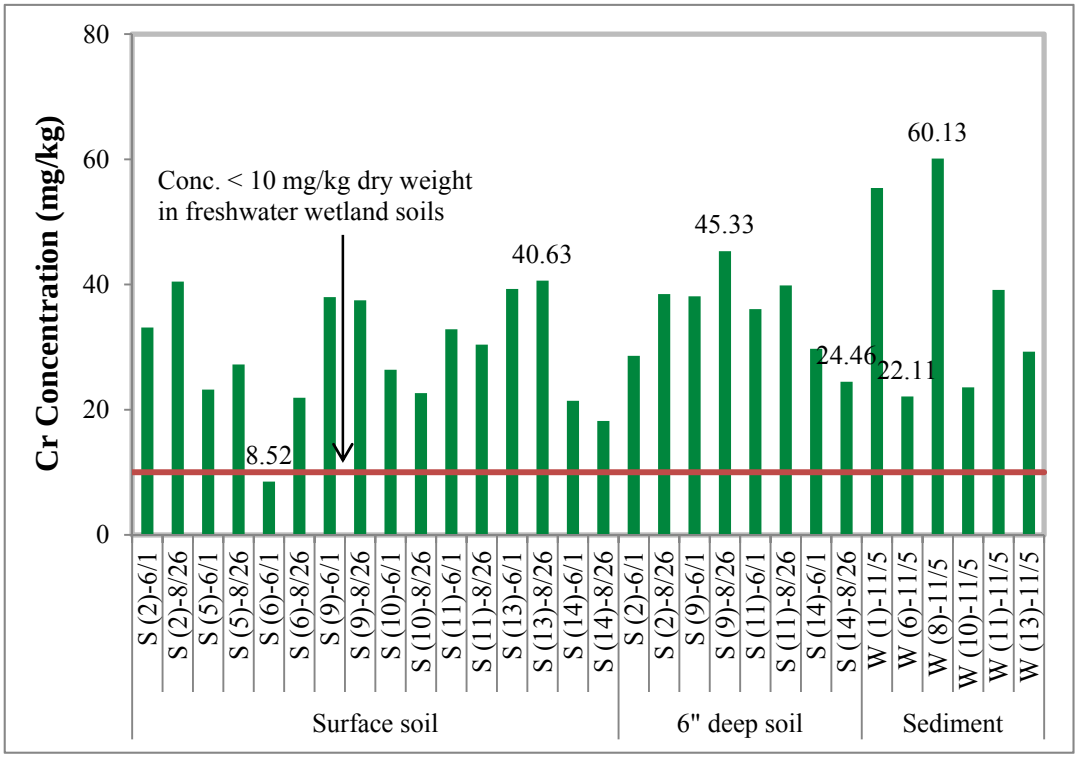


Figure 66: Variations of chromium at specific sites during the study period

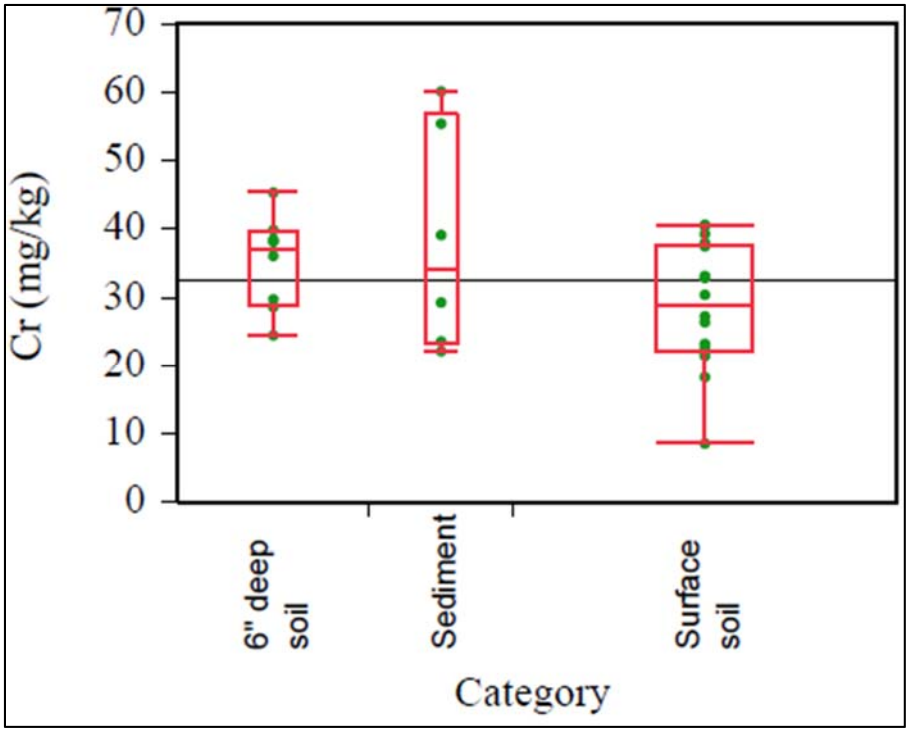


Figure 67: Distributions of chromium in different sample categories

Copper (Cu)

Copper serves as an essential micronutrient for plants and animals when present in significant concentrations. In surface water, it is usually present as chelated compounds of Cu (II). It forms insoluble complexes with hydroxides, sulfides, and carbonates. In many cases, it is used as a biocide to control algae and other plants. In aquatic environments, it may have low toxicity to benthic organisms and fish at 500 µg/L concentration. It may also induce toxicity to some cyanobacteria at concentrations less than 5-10 µg/L (Kadlec & Knight, 1996).

In all tested samples, the minimum and maximum concentrations of copper were 2.69 mg/kg and 19.37 mg/kg, respectively with an average concentration of 10.59 ± 0.85 mg/kg (Table 12). The study also showed various ranges of copper concentrations tested in three different sample categories; such as 2.69-15.33 mg/kg in the surface soil, 3.05-17.52 mg/kg in the sediment, and 6.41-19.37 mg/kg in the 6" deep soil (Figure 68, Table D1 from Appendix D). The distributions of Cu in the tested samples were in the following order: 6"deep soil > sediment > surface soil. However, the statistical analysis did not show any significant difference in their distributions ($p>0.05$) (Figure 69, Table E3 from Appendix E).

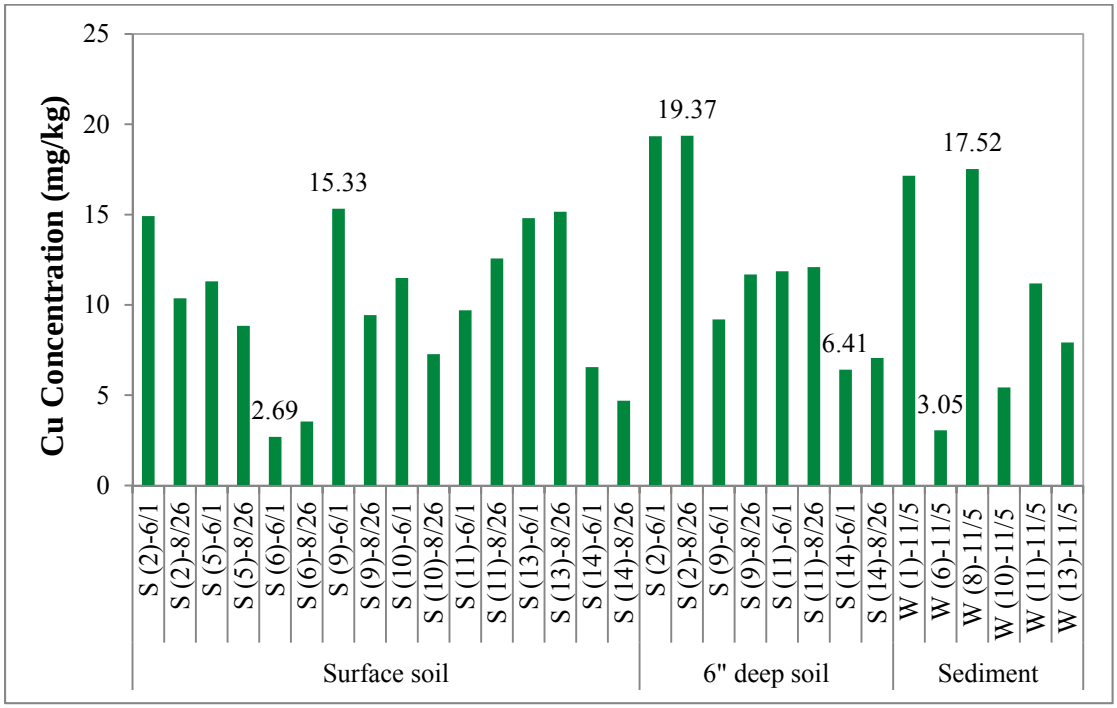


Figure 68: Variations of copper at specific sites during the study period

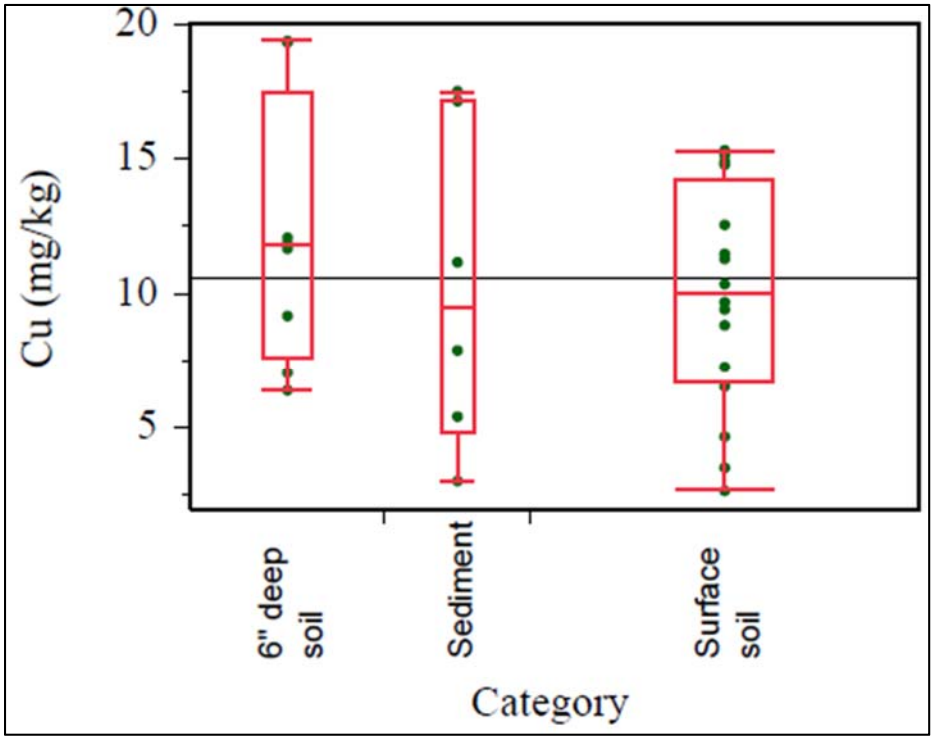


Figure 69: Distributions of copper in different sample categories

Nickel

Nickel is generally associated with suspended particles and organic matter, and occurs as precipitates in surface waters. In the environment, it appears as ores of sulfides, arsenides, silicates, oxides, etc. Industrial activities are among the major sources of nickel discharge into the environment. Average concentration of nickel in agricultural soils is about 40 mg/kg dry weight, and the background concentration of nickel in wetland areas is typically less than 25 mg/kg dry weight (Kadlec & Knight, 1996; Weiner, 2000).

In this study, the overall concentrations of nickel ranged from 7.22-45.94 mg/kg with an average of 21.44 ± 1.59 mg/kg (Table 12). At the specific sites, the distributions

of nickel are presented in Figure 70 and Table D1 (Appendix D). It is clear from the figure that the concentrations ranged from 7.22-34.28 mg/kg in the surface soil, 8.05-25.77 mg/kg in the sediment, and 18.09-45.94 mg/kg in the 6" deep soil. Among the three categories of samples, the 6" deep soil showed relatively high concentrations than the other two. One way ANOVA also showed weakly significant difference in the distribution of Ni concentrations among the sample categories ($p<0.05$) (Figure 71, Table E3 from Appendix E).

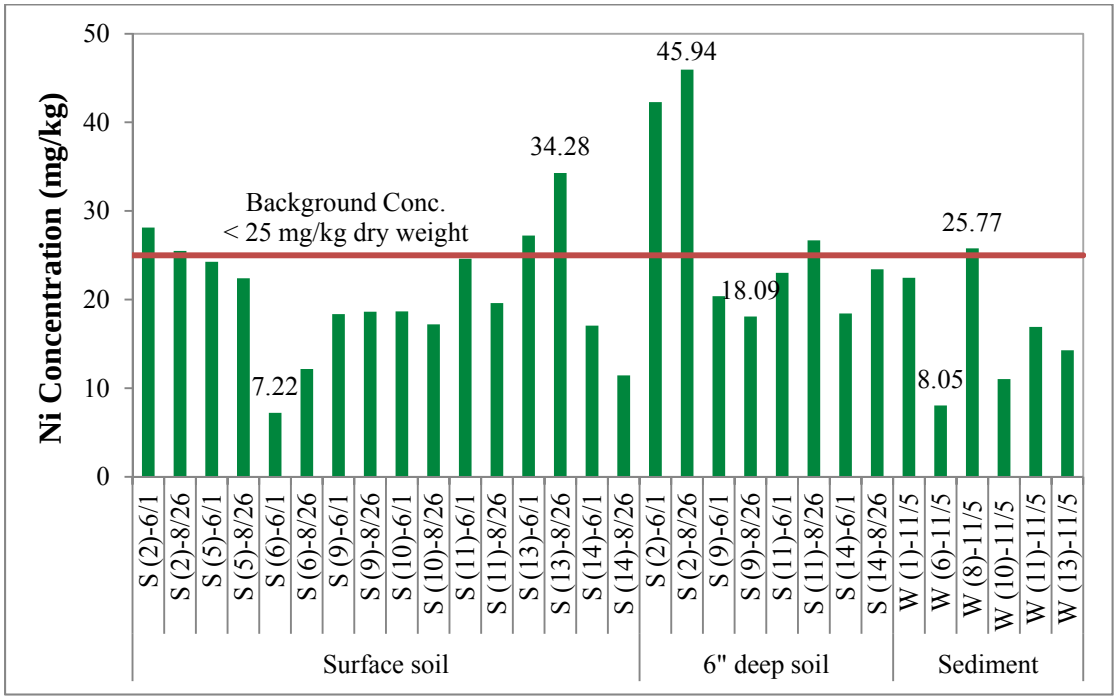


Figure 70: Variations of nickel concentrations at specific sites during the study period

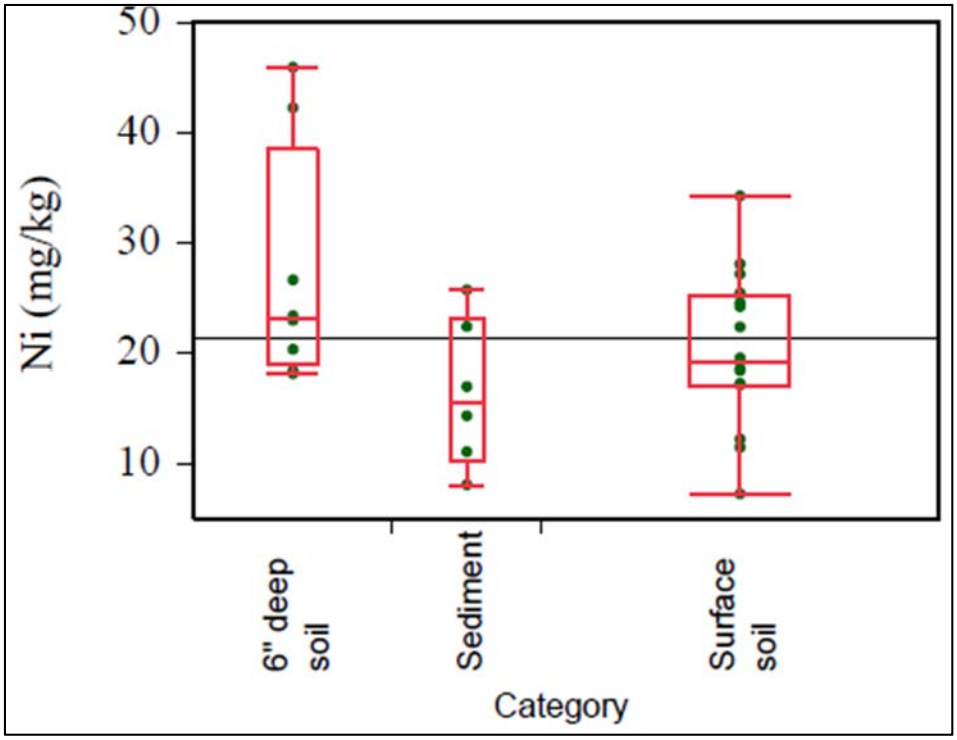


Figure 71: Distributions of nickel in three different sample categories

Lead (Pb)

Lead is usually not a very mobile metal and is likely to be retained in the upper soil in certain environmental conditions. There could be a chance of undergoing speciation to the more insoluble sulfate, oxide, and phosphate salts (Weiner, 2000). Minerals of lead are mostly seen in igneous, metamorphic, and sedimentary rocks. In natural surface waters, levels of dissolved lead are generally low, and they mostly appear as divalent Pb (II) which forms salts with sulfides, carbonates, sulfates, and chlorophosphates (Kadlec & Knight, 1996; Weiner, 2000). Naturally, it enters the environment through weathering of minerals. However, some of the anthropogenic sources may include mining and smelting of lead and its associated metals, combustion of

fossil fuels and municipal sewage, dumping of commercial products such as lead-acid storage batteries, paints, ammunition, glassware, solder, piping, cable sheathing, roofing, etc. (Weiner, 2000). Agricultural soils contain an average Pb concentration of 10 mg/kg dry weight, though it is found as less than 40 mg/kg dry weight in background wetland soils (Kadlec & Knight, 1996).

This study showed Pb concentrations ranging from 6.52-26.09 mg/kg with an average of 15.59 ± 0.80 mg/kg (Table 12). From Figure 72 and Table D1 (Appendix D), it is clear that there is no significant difference in the distribution of lead; such as 6.52-26.09 mg/kg in the surface soil, 12.40-22.39 mg/kg in the 6" deep soil, and 8.08-19.35 mg/kg in the sediment.

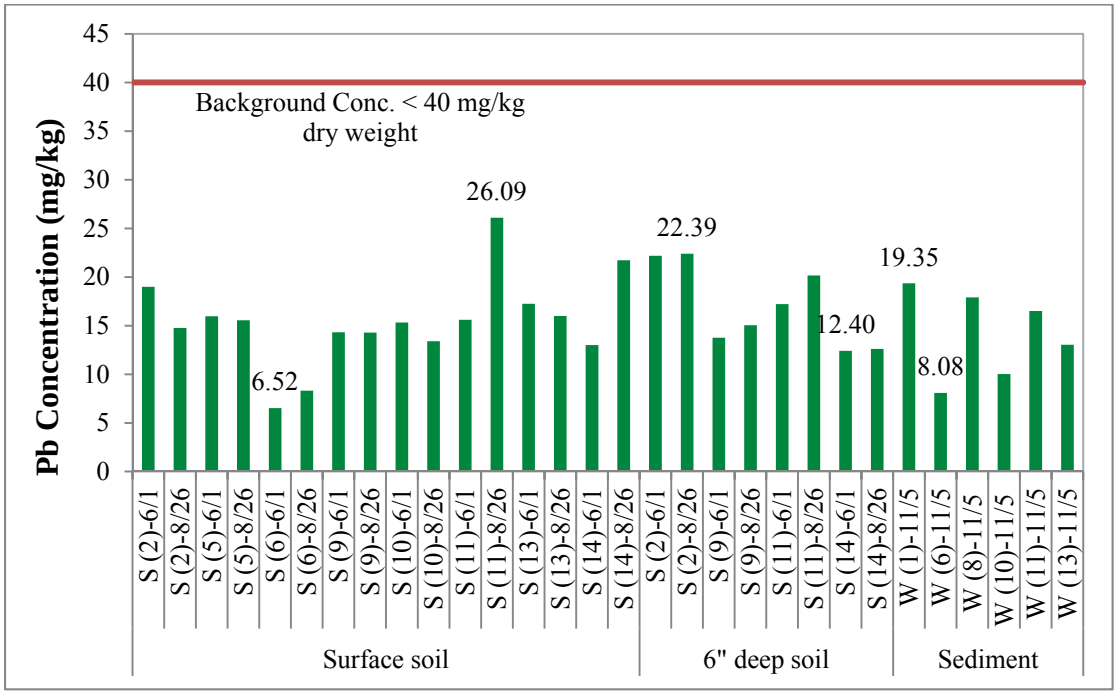


Figure 72: Variations of lead at specific sites during the study period

Although the surface soil showed relatively high Pb concentrations than the sediment and the 6” deep soil, one way ANOVA test did not show any significant differences in Pb distributions among the three sample categories ($p>0.05$) (Figure 73, Table E3 from Appendix E).

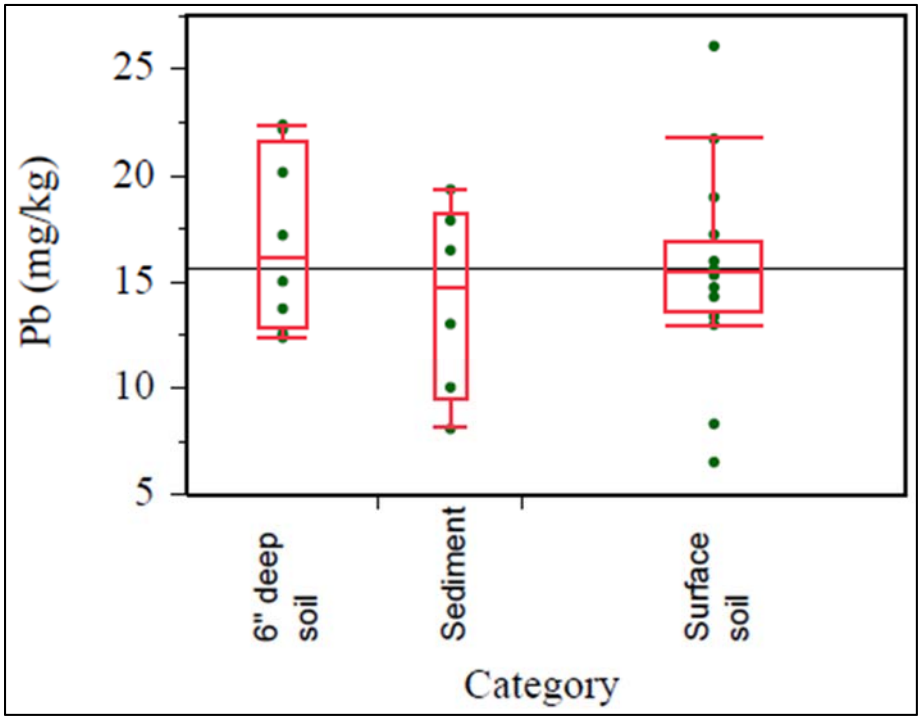


Figure 73: Distributions of lead in three different sample categories

Zinc (Zn)

Zinc serves as an essential element for both plants and animals in their respiration and photosynthetic activities. It is usually present as divalent Zn (II) in surface waters, where it forms complexes with hydrates, carbonates, and organics. In natural waters, it is usually present in both suspended and dissolved forms. The most obvious sources for

zinc in the environment include industrial waste water, agricultural runoff, zinc and brass plating, ground wood pulp, newsprint paper, etc. Agricultural soils contain an average of 80 mg/kg dry weight, and it is typically less than 120 mg/kg dry weight in wetland soil (Kadlec & Knight, 1996; Weiner, 2000).

In this study, the concentrations of zinc ranged from 14.47-82.61 mg/kg with an average of 49.77 ± 3.17 mg/kg (Table 12). All sites showed zinc concentrations less than the background concentration found in wetland soils (120 mg/kg dry weight). The results did not show measurable variations in zinc concentrations among the three sample categories. It ranged from 14.47-66.29 mg/kg in the surface soil, 33.21-82.61 mg/kg in the 6" deep soil, and 17.79-76.15 mg/kg in the sediment (Figure 74, Table D1 from Appendix D). Although, the 6" deep soil had relatively high concentration than the sediment and the surface soil, one way ANOVA analysis did not show any significant differences in the distributions of Zn among the three sample categories ($p>0.05$) (Figure 75, Table E3 from Appendix E).

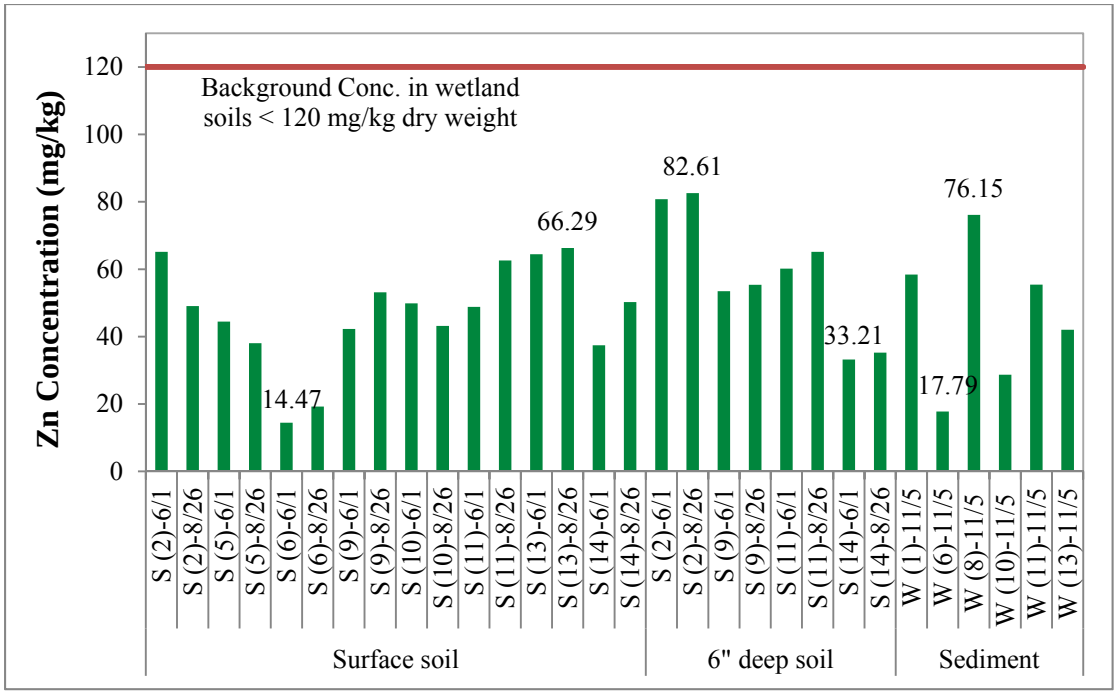


Figure 74: Variations of zinc at specific sites during the study period

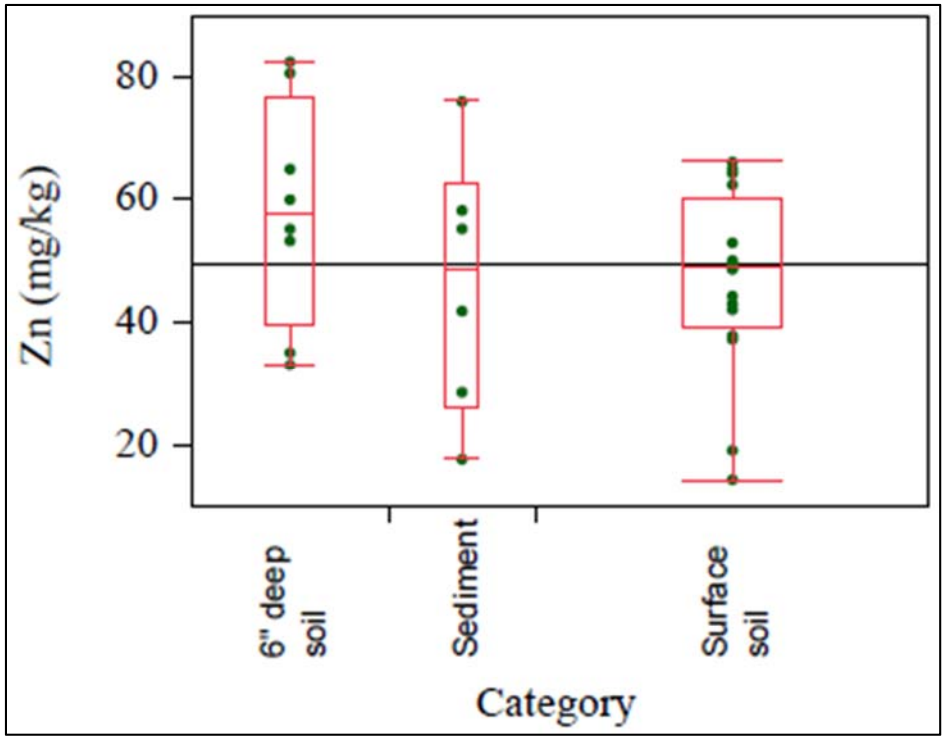


Figure 75: Distributions of zinc in different sample categories

After analyzing the heavy metals in the wetland soils, most of them are found to be at or below the acceptable concentrations, indicating no immediate concern for metal toxicity in the system. The summary of metal distributions among the three different soil categories is given in Table 13. The accumulation for most of the heavy metals is the highest at 6" depth. This could mean that the wetland intercepts metals in the sub-surface that slowly undergo degradation process over time. The degradation mechanism also reduces metals from the surface that otherwise could have reached the nearby water bodies through overland flow.

Table 13: *Summary of heavy metal distribution in three different soil categories*

Metals	**Surface**	**6”deep soil**	**Sediment**
Fe		High	
Mn		High	
As		High	
Co		High	
Cr			High
Cu		High	
Ni		High	
Pb	High		
Zn		High	

Dye Tracer Experiment

One of the major objectives of this study was to investigate and understand the flow regime connecting the surrounding agricultural fields to the wetland. In the wetland areas, the sub-surface flow usually remains active and serves as the recharge area for the wetland. The agricultural fields that surround wetlands are generally expected to serve as the recharge area for them. In order to determine the sub-surface flow, dye tracer experiments are considered a convenient and accurate method since the measure of such flow directly is difficult. In this study, tracer experiments were conducted by using fluorescein dye and bromide to model the sub-surface flow. Spatial and temporal movement of tracers was monitored over 3 days. Additional samplings were conducted during rain events.

The experiment was set up in an area on the southern end of the wetland since the flow was from north to south within the wetland. Six holes were drilled in which two were used as injection holes and the remaining four were used as observation holes for monitoring tracer migration. Following the injection of fluorescein dye and bromide, water samples were collected for 3 days from each of the four observation holes at the interval of 2-3 hours on the first day, every 4 hours on the second day, and at three different times on the third day. All water samples were scanned for fluorescein dye and bromide by using the Shimadzu RF-5301 PC Spectrofluorophotometer and the Ion Chromatograph in the Hydrology Laboratory at UNI. Neither fluorescein nor bromide was detected in any of the water samples collected from both the observation holes and the surface water body. Figure 76 shows the fluorescein detection peak in one of the

tested samples. It is clear from Figure 76 that the fluorescein standard showed the detection peak in the range of 508 to 511.7 nm (which is an acceptable emission wavelength). None of the samples had any detection in that range.

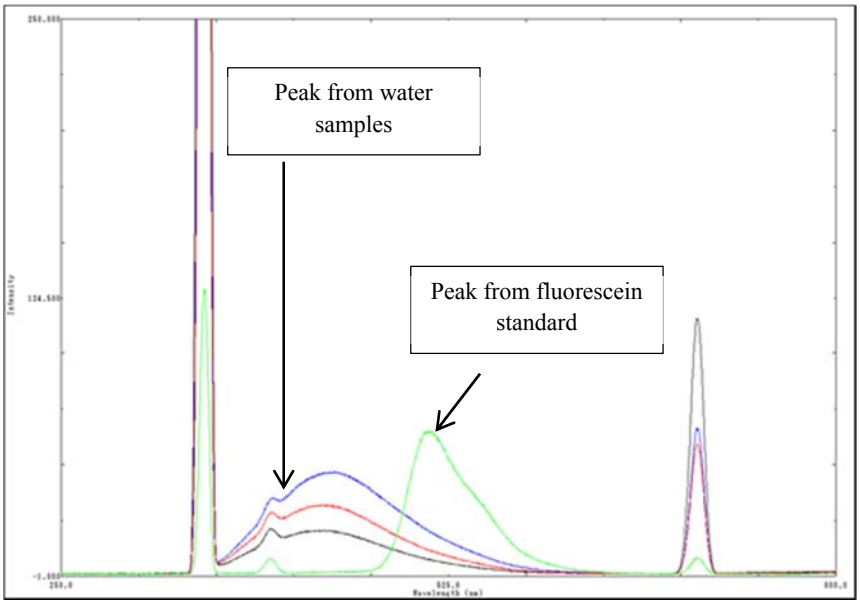


Figure 76: Detection of peaks during the analysis

Although the initial dye tracer experiment did not detect fluorescein and bromide in any of the water samples, the following conclusions could be drawn based on the sub-surface soil characteristics and the hydrological settings of the wetland:

- The tracers may have entered the sand lenses and became immobilized. (Scenario-1)
- The tracers may have moved toward the wetland's water body in a curved path below the hole bottoms. (Scenario-2)
- The tracers may have been lost to deep infiltration. (Scenario-3)

Not to scale

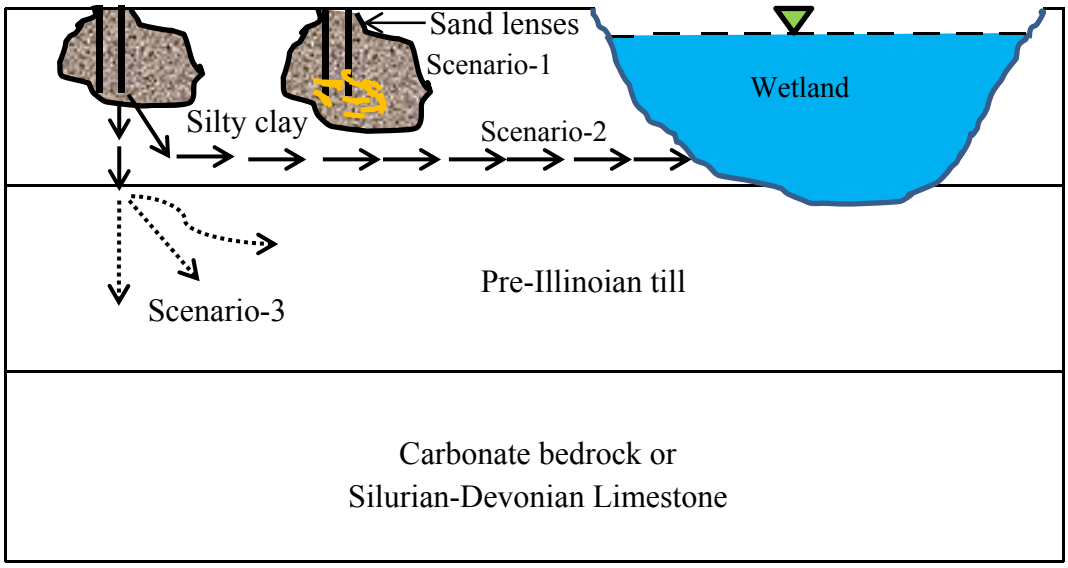


Figure 77: Conceptualized model of tracers' movement depicting the sub-surface flow path in the study area

The conceptualized model (Figure 77) depicts the three different sub-layers; silty clay, pre-Illinoian till, and carbonate bedrock. Silty clay, also known as loamy sediments, is a mixture of silt, clay, and some sand deposited from high topographic positions, and is formed during the interglacial period. It may vary from less than a meter to several meters thick. The sediment is moderately well-drained to poorly drained loamy soils. The soil forming processes and the presence of plant roots make this layer to contain macropores, which play important roles in altering the vertical flow of water. Pre-Illinoian till is a semi-confining layer having a hydraulic conductivity of 10^{-8} to 10^{-7} m/s (Iqbal, 2000). The Silurian-Devonian bedrock is a layer of limestone and dolomite with interbedded layers of shales and evaporites. The thickness of this layer may vary from 300 to 400 feet in Iowa. The permeability rate for different layers of underlying bedrock

usually varies from low, medium to high, primarily caused by the presence of shale units (Sedlacek, 2010).

It is generally expected that loamy sediments and sandy soil layers connect agricultural fields to the wetland. Existence of such layers might create a preferential flow path, and serve as the recharge area for the wetland. Although the dye tracer experiment did not support the stated hypothesis, the most likely scenarios are modeled in Figure 77. In Scenario-1, the tracers while flowing through the silty clay layer are caught up in the discontinuous sand lenses and became immobile due to permeability differences. This phenomenon is likely to occur given the hydrological settings of the wetland. In Scenario-2, the tracers may have moved below the levels of the monitoring wells toward the wetland's large water body to the south. Therefore, none of the wells detected any tracers. In Scenario-3, the tracers may have moved vertically into the Pre-Illinoian till and got trapped due to the very low permeability of the unit. The chances are high that the tracers may have been lost to infiltration this way. Besides, the rainfall that took place during the experiment probably did not exert adequate fluid pressure in the pore spaces to initiate any tracer movement in the short term. The rainfall to some extent might have diluted the tracers below detection limits.

CHAPTER 6

CONCLUSIONS

Because of rapid urbanization and agricultural practices, assessment of wetlands is necessary not only to determine the quality of water that flows through them, but also to make sure that they are well protecting the hydrological environment from natural contaminants.

The main purpose of this study was to determine how well the Beaver Valley Wetland system functions to filter contaminants coming from the surrounding areas. Altogether 78 water samples and 84 soil samples were collected from May through November in order to assess the natural cycle of the wetland. The sampling period was divided into segments like early summer (May 5, June 1, and June 22), mid-summer (July 15, July 31, and August, 26), and late summer (September 23, October 14, and November 5). The analysis of different soil categories (surface soil, 6" deep soil, and sediment) did not show high accumulation of heavy metals in soil, indicating no immediate concern for metal toxicity in the wetland environment. Most metals are found to be at or below the acceptable concentrations. The study also addressed the sub-surface flow, which is generally expected to serve as the primary recharge mechanism for the wetland. Tracer analysis conducted for the sub-surface flow in this study did not prove the stated hypothesis. Although the study could not find an active shallow sub-surface flow, the tracers may have entered the sand lenses and became immobilized or have moved in a curved flow path deeper than the injection holes. Alternatively, the tracers may have been lost to deep infiltration. The tracer experiment should be modified in future studies by

installing more monitoring wells and conducting more frequent tracer injections. In such experiments, higher volumes of tracers are recommended.

Among the several water quality parameters studied, turbidity, total suspended solids, dissolved oxygen, biochemical oxygen demand, chloride, nitrate, phosphorus, and *E. coli* were of major concerns. The observed water quality in the Beaver Valley Wetland demonstrates that the unit is capable of filtering incoming contaminants. Most contaminants showed significant decrease in their concentrations going from the inlet to the outlet. There were significantly high concentrations at inlet sites W1, W2, and W3. High turbidity, high load of TSS, and low DO were prominent at these sites throughout the study period. This was expected because these sites are characterized by high organic load with hardly any water, and there was not much turbulence in the water column. It is also possible that these sites received high sediments from the surrounding areas, thereby making significant variations in the water quality. Although the water samples at the inlet sites were much degraded, the quality significantly improved toward the outlet sites. Besides, the DO level increased going from the inlet to the outlet. The study showed that the wetland has the capability to replenish oxygen despite high BOD and high water temperature.

The wetland being in proximity to the agricultural fields, the study of nitrate, chloride, and phosphorus are considered very important to understand the system's effectiveness in filtering these contaminants. Given the topographic setting, there is a high possibility of agricultural contaminants being flushed into the wetland. Interestingly,

none of the sites showed dissolved nitrate in the water, possibly meaning that nitrates served as an electron acceptor during the process of denitrification. This process is likely to predominate in this kind of ecosystem where there is high organic matter and less dissolved oxygen, causing microorganisms to extract oxygen from nitrates to decompose the organic matter. Such mechanisms of denitrification would be interesting to study in the future. On the other hand, phosphorus concentrations were episodically higher mostly at inlet sites (mainly W1, W2, W3, and W4) than in the other sites throughout the study period. The study showed that the phosphorus concentrations decreased at the outlet, indicating that the wetland has been effectively removing phosphorus from the water column. Relatively less phosphorus content in the sediment samples compared to water also indicates that the wetland has not been saturated with phosphorus. Because agricultural fields are close to the wetland, long-term monitoring of phosphorus in both the sediments and the water is highly recommended. The concentrations of chloride were found to be well below the levels of concern. However, the spatial distribution clearly indicated significantly less chloride concentrations in the outlet sites compared to the inlets.

The quality of water changed significantly during mid-summer compared to early and late summer. Most of the parameters showed high concentrations during mid-summer. Some of the factors like rainfall, algae growth, and high organic load have played significant roles in affecting the water quality. In particular, the rainfall and the algae growth were found to affect the water quality during mid-summer. The rain events that started to pick up in early summer had brought in more contaminants into the

wetland from the surroundings, thereby creating favorable conditions for algae to grow. Therefore, during mid-summer the mat of algae was clearly visible. The effect of rainfall and algae growth was prominent at most of the sites. Although the study showed variations in WQI from “medium” to “good” category, a sudden drop in WQI with increasing rainfall was evident. This was probably due to the flushing of contaminants into the wetland from the surrounding fields.

The findings of this project clearly explained the performance of the Beaver Valley Wetland in the environment. It is evident from the study that the wetland has been functioning well in filtering various contaminants. Since there is high input of contaminants from the surrounding fields (especially agricultural fields), better management practices should be focused on these fields to protect the unique function of the wetland ecosystem. In order to get a complete picture of the wetland, the water quality monitoring should be continued and compared over multiple years. It would be interesting to compare the performance of the wetland between the growing and the non-growing seasons. Sampling of water from different depth profiles of the wetland are recommended for future water quality monitoring plans. Also, additional sites should be considered to have a better sampling distribution.

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APPENDIX A

WATER QUALITY DATA

Table A1. Field and laboratory data of the water quality parameters

pH

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		31.5	20.0	22.37	21.63	16.67	13.5	9.99	8.2
W2		29.4	19.8	22.07	22.4	18.77			
W3		32.4	21.1	24.23	22.67	18.27	14.5	10.1	8.7
W4	18.63	33.9	21.73	27.9	24.4	22.07			
W5	8.16	28.4	21.83	29.4	27.13	23.7			
W6	8.23	22.8	21.27	27.6	27.7	23.17	15.6	10	6.8
W7	7.97	24.9	21.88	30.07	26.9	24.57			
W8	8.36	23.4	22.23	29.4	28.23	24.07	16.1	9.6	7.3
W9	8.23	24.0	22.03	30.73	27.77	24.37			
W10							15.7	12.2	7.4
W11							14.2	12.7	7
W12							14.7	12.9	7.6
W13							15.1	13.2	7.2

Temperature (°C)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		7.80	6.14	6.80	6.23	6.420	7.86	7.74	8.01
W2		8.22	6.45	6.58	6.53	6.31			
W3		6.80	7.16	6.58	6.51	6.59	7.96	8.98	8.64
W4	7.66	10.91	9.21	7.38	7.13	7.01			
W5	8.16	8.69	9.52	8.82	8.91	8.77			
W6	17.77	22.80	21.27	27.60	27.70	23.17	15.60	10.00	6.80
W7	16.53	24.90	21.88	30.07	26.90	24.57			
W8	16.33	23.40	22.23	29.40	28.23	24.07	16.10	9.60	7.30
W9	16.13	24.00	22.03	30.73	27.77	24.37			
W10							15.70	12.20	7.40
W11							14.20	12.70	7.00
W12							14.70	12.90	7.60
W13							15.10	13.2	7.2

Electrical Conductivity (µs/cm)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		233	218	290	304	330	351	379	428
W2		336	330	371	347	347			
W3		442	280	388	430	425	393	385	425
W4	258	313	251	340	320	407			
W5	301	301	202	271	213	224			
W6	242	207	204	213	200	202	244	287	185
W7	267	255	254	227	224	192			
W8	247	232	204	183	187	189	195	261	200
W9	244	235	201	185	188	185			
W10							162	187	185
W11							162	190	197
W12							162	188	208
W13							173	187	204

Total Dissolved Solids (ppm)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		161	150	200	212.67	224	241	262	288
W2		232	228	256	239.67	239			
W3		305	193	267.49	295.67	292.33	273	265	293
W4	178	216	173	235	221.67	281			
W5	208	208	140	187	144.33	154.33			
W6	167	143	141	147	136.67	138.67	169	198	130
W7	184	176	175	157	153.33	132.33			
W8	170	160	141	127	129	130.33	126	182	138
W9	168	162	139	128	127.81	128			
W10							113	129	129
W11							113	130	135
W12							104	126	143
W13							122	129	135

Turbidity (NTU)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		4.51	10.67	23.60	29.47	82.23	238.00	47.20	33.90
W2		11.50	6.96	32.70	16.67	11.55			
W3		12.23	22.73	18.37	30.73	34.87	34.80	18.00	23.50
W4	11.42	14.300	8.72	9.29	27.60	43.03			
W5	26.10	7.710	5.91	7.18	22.63	20.33			
W6	8.71	4.73	3.89	6.54	15.90	3.78	14.70	18.30	15.70
W7	8.71	9.74	12.60	4.84	11.75	18.67			
W8	11.10	3.16	6.37	4.89	3.90	10.90	20.20	22.60	24.60
W9	13.43	2.50	12.30	10.07	9.18	207.00			
W10							4.33	15.80	11.10
W11							5.71	16.50	21.10
W12							5.00	12.90	8.41
W13							13.40	6.71	11.4

Total Suspended Solids (mg/L)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		36.00	86.44	154.54	358.00	211.80	366.25	193.19	28.00
W2		20.70	7.26	31.33	13.25	17.50			
W3		15.55	19.86	21.28	40.25	24.42	45.00	18.33	18.33
W4	39.57	50.00	8.37	30.62	80.22	192.57			
W5	14.69	17.55	5.44	11.87	17.16	18.00			
W6	23.70	7.10	19.50	4.70	4.37	2.50	6.66	15.40	9.80
W7	68.48	19.37	12.66	36.50	46.87	108.00			
W8	23.73	1.50	5.30	6.50	5.00	19.14	15.86	15.00	19.20
W9	24.28	2.50	16.33	25.10	48.25	426.16			
W10							15.00	15.55	16.40
W11							11.37	11.55	12.20
W12							7.37	16.66	3.40
W13							20.40	6.66	14.00

Dissolved Oxygen (mg/L)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		7.86	3.88	1.48	1.25	1.40	5.00	6.92	11.60
W2		16.35	3.34	2.17	1.43	1.84			
W3		4.20	5.98	3.57	2.13	2.56	9.88	12.85	14.31
W4	8.92	18.47	13.57	16.25	6.50	12.50			
W5	11.84	17.96	14.89	15.16	11.53	8.64			
W6	10.01	20.14	11.09	15.05	3.69	5.78	12.43	8.54	13.34
W7	9.58	21.33	14.42	17.28	5.40	12.38			
W8	10.47	20.23	8.18	15.60	4.78	9.67	10.70	9.60	13.78
W9	10.40	19.80	9.03	14.05	6.35	8.19			
W10							9.91	3.50	12.44
W11							12.67	3.98	13.23
W12							13.50	8.95	17.43
W13							6.47	7.77	12.56

Biochemical Oxygen Demand (mg/L)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1		5.70	2.97	0.67	0.30	0.49	4.71	5.46	9.59
W2		7.47	1.27	1.00	0.20	0.84			
W3		2.57	4.69	2.90	0.58	1.93	8.89	11.68	6.68
W4	3.29	17.16	12.56	14.59	4.79	11.85			
W5	6.12	5.42	8.51	6.58	9.50	7.27			
W6	5.80	7.27	7.49	4.16	1.61	4.64	3.83	2.80	4.65
W7	3.55	20.17	11.83	11.61	3.80	11.19			
W8	3.91	8.14	5.79	5.20	2.43	7.81	1.95	4.17	2.42
W9	3.51	7.03	6.85	10.36	4.57	7.03			
W10							2.14	2.44	2.53
W11							2.76	1.99	3.07
W12							10.48	2.65	7.57
W13							5.05	1.82	4.8

Chloride (mg/L)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1	10.33	10.21	7.24	20.65	24.860	23.07	19.70	31.06	47.56
W2	31.23	13.96	13.98	26.64	15.79	17.33			
W3	19.50	18.560	15.90	20.82	25.18	24.39	16.89	21.12	14.43
W4	8.19	8.50	7.34	9.48	13.85	10.42			
W5	10.60	11.81	10.16	15.86	13.35	15.91			
W6	8.71	8.43	8.38	13.71	11.67	11.83	8.09	11.24	9.88
W7	9.65	7.28	10.48	17.98	15.14	12.20			
W8	8.81	7.66	8.14	8.80	9.03	12.22	8.14	10.96	9.84
W9	8.87	7.69	8.55	8.77	9.17	12.34			
W10							8.27	9.00	9.86
W11							8.30	9.10	9.86
W12							7.97	14.04	10.29
W13							20.42	13.55	14.79

Sulfate (mg/L)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1	7.83	6.91	2.63	2.03	2.11	8.80	12.52	19.92	38.73
W2	18.05	13.62	13.69	16.74	22.13	22.50			
W3	16.74	20.17	8.82	10.09	15.73	20.52	21.85	20.27	26.37
W4	8.90	4.52	0.80	ND	0.90	1.12			
W5	13.25	8.30	6.12	21.30	23.22	28.53			
W6	8.26	4.75	2.74	6.54	5.74	3.62	7.54	7.05	5.14
W7	10.53	2.89	0.95	ND	1.01	2.79			
W8	8.02	4.92	1.92	1.67	1.09	3.65	4.73	7.93	4.97
W9	7.91	4.84	1.83	1.68	1.12	3.81			
W10							2.57	3.19	4.70
W11							2.83	3.15	4.70
W12							4.27	4.96	6.49
W13							0.82	5.21	9.07

Nitrate (mg/L)

ND: Not Detected

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1	ND	ND	ND	ND	ND	ND	ND	ND	ND
W2	ND	ND	ND	ND	ND	ND			
W3	ND	ND	ND	ND	ND	ND	ND	ND	ND
W4	ND	ND	ND	ND	ND	ND			
W5	ND	ND	ND	ND	ND	ND			
W6	ND	ND	ND	ND	ND	ND	ND	ND	ND
W7	ND	ND	ND	ND	ND	ND			
W8	ND	4.92	ND	ND	ND	ND	ND	ND	ND
W9	4.27	ND	ND	ND	ND	ND			
W10							ND	ND	ND
W11							ND	ND	ND
W12							ND	ND	ND
W13							ND	ND	ND

Ammonia (mg/L)

NA: Not Available

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1	NA	0.40	0.04	0.08	0.98	0.42	0.11	0.12	0.00
W2	NA	0.28	0.01	0.08	0.04	0.08			
W3	NA	19.50	0.250	0.01	0.060	0.10	0.37	0.40	0.00
W4	0.33	0.07	0.00	0.16	0.02	2.75			
W5	0.19	0.11	0.01	0.09	0.02	0.12			
W6	0.38	0.20	0.01	0.12	0.08	0.16	0.10	0.40	0.00
W7	0.46	0.08	0.02	0.07	0.63	1.26			
W8	0.43	0.19	0.01	0.06	0.06	0.28	0.12	0.21	0.01
W9	0.43	0.28	0.01	0.09	0.05	0.26			
W10							0.05	0.15	0.02
W11							0.08	0.12	0.00
W12							0.08	0.11	0.00
W13							0.08	0.06	0.03

Phosphorus (µg P/L)

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1	559.00	213.00	477.33	382.00	342.67	1712.86	339.24	97.14	185.67
W2	1363.67	232.33	196.33	370.33	172.67	300.33			
W3	1564.00	193.33	401.67	753.33	415.67	317.00	185.00	682.57	198.33
W4	363.33	312.33	1330.67	893.33	1468.67	567.67			
W5	263.67	223.00	381.00	376.67	319.00	254.33			
W6	231.00	284.00	486.00	277.00	328.33	233.33	182.00	264.00	236.33
W7	328.00	702.33	503.67	463.00	1241.67	565.00			
W8	206.00	207.67	452.00	403.67	315.67	331.67	187.33	104.29	191.67
W9	265.00	167.33	491.33	378.67	390.67	326.67			
W10							157.67	214.00	221.67
W11							257.67	228.67	181.67
W12							233.67	236.33	138.00
W13							1264.29	195.67	130.67

E. coli (CFU)

NA: Not Available

Sites	May 5	Jun 1	Jun 22	Jul 15	Jul 31	Aug 26	Sept 23	Oct 14	Nov 5
W1	NA	0	160	0	0	0	0	0	0
W2	NA	20	0	40	20	20			
W3	NA	0	60	0	0	0	0	80	80
W4	80	0	60	0	40	0			
W5	0	0	40	0	0	0			
W6	20	0	0	0	0	100	100	40	0
W7	20	0	20	0	0	120			
W8	0	0	40	100	40	40	140	100	0
W9	20	0	0	160	400	0			
W10							120	40	0
W11							20	60	40
W12							0	0	0
W13							20	40	300

Table A2: Monthly average data for physical water quality parameters

Statistics	**pH**	**Temp (ºC)**	**EC (µs/cm)**	**TDS (ppm)**	**Turbidity (NTU)**	**TSS (mg/L)**	**DO (mg/L)**	**BOD (mg/L)**
May 5	8.10± 0.10	16.77± 0.49	259.83± 9.09	179.16± 6.35	13.25± 2.67	32.41± 7.92	10.20± 0.40	4.36± 0.51
June 1	9.32± 0.50	27.85± 1.40	283.77± 24.51	195.88± 16.91	7.82± 1.43	18.92± 5.25	16.26± 2.01	8.99± 1.92
June 22	8.33± 0.44	21.31± 0.29	238.22± 14.92	164.44± 10.26	10.01± 1.87	20.13± 8.50	9.37± 1.47	6.88± 1.25
July 15	8.36± 0.50	27.08± 1.11	274.22± 26.12	189.38± 17.96	13.05± 3.24	35.82± 15.30	11.17± 2.21	6.34± 1.62
July 31	7.58± 0.34	24.42± 0.88	268.11± 28.63	184.53± 19.98	18.64± 3.17	68.15± 37.16	4.78± 1.07	3.08± 0.99
Aug 26	7.59± 0.33	21.74± 1.00	277.88± 32.99	191.11± 22.64	48.04± 21.38	113.45± 47.29	6.99± 1.44	5.89± 1.40
Sept 23	8.99± 0.27	14.92± 0.30	230.25± 32.66	157.62± 22.95	42.01± 28.22	60.99± 43.81	10.07± 1.06	4.97± 1.11
Oct 14	8.49± 0.22	11.33± 0.54	258.00± 30.24	177.62± 21.06	19.75± 4.24	36.54± 22.41	7.76± 1.07	4.12± 1.16
Nov 5	9.33± 0.25	7.52± 0.22	254.00± 37.75	173.87± 25.50	18.71± 3.04	15.16± 2.57	13.58± 0.62	5.16± 0.91

Note:
Temp = Temperature; EC = Electrical Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; BOD = Biochemical Oxygen Demand

APPENDIX B

SUMMARY STATISTICS

Table B1. Physical water quality parameters during the study period

Statistics	**pH**	**Temp (ºC)**	**EC (µs/cm)**	**TDS (ppm)**	**Turbidity (NTU)**	**TSS (mg/L)**	**DO (mg/L)**	**BOD (mg/L)**
Minimum	6.14	6.80	162.00	104.00	2.50	1.50	1.25	0.20
Maximum	10.91	33.90	442.00	305.00	238.00	426.16	21.33	20.17
Mean	8.45	19.75	261.02	179.68	21.35	45.39	9.99	5.92
SEM	0.14	0.83	9.11	6.23	4.14	9.42	0.60	0.48
Std. Deviation	1.21	7.18	78.93	54.52	35.82	81.58	5.23	4.16
Median	8.63	21.63	235.00	162.00	12.30	18.00	9.91	5.74
Variance	1.46	51.66	6231.29	2973.07	1283.32	6656.47	27.41	17.33

Note:
Temp = Temperature; EC = Electrical Conductivity; TSS = Total Suspended Solids; DO = Dissolved Oxygen; BOD = Biochemical Oxygen Demand; SEM = Standard Error Mean

Table B2. Bacteriological & Chemical water quality parameters during the study period

Statistics	***E. coli* (CFU)**	**Chloride (mg/L)**	**Sulfate (mg/L)**	**Ammonia (mg/L)**	**Phosphorus**	
					Water	***Sediment***
Minimum	0	7.24	0.80	0.00	97.14	91.46
Maximum	400	47.56	38.73	2.75	1712.86	794.02
Mean	37	13.65	8.78	0.19	418.13	314.44
SEM	7.76	0.781	0.911	0.042	40.04	29.50
Std. Deviation	67.24	6.90	7.94	0.36	353.63	164.28
Median	0	11.10	10.18	0.08	314.00	262.67
Variance	4522.52	47.63	47.40	0.13	125056.54	26990.77

Note:
SEM = Standard Error Mean

APPENDIX C

TOTAL PHOSPHORUS ANALYSIS

Table C1. Results of total phosphorus analysis in soils and sediments

	Site	Phosphorus (µgP/g dry weight)
SURFACE SOIL	S1-7/31	794.02
	S2-6/1	386.60
	S2-8/26	340.35
	S5-6/1	341.24
	S5-8/26	411.78
	S6-6/1	91.46
	S6-8/26	121.32
	S9-8/26	219.91
	S10-6/1	337.97
	S10-8/26	256.74
	S11-6/1	239.95
	S11-8/26	286.18
	S13-6/1	422.79
	S13-8/26	452.05
	S14-6/1	283.13
	S14-8/26	262.67
6" DEEP SOIL	S2-6/1	398.28
	S2-8/26	488.16
	S9-6/1	208.82
	S9-8/26	212.27
	S11-6/1	233.60
	S11-8/26	197.49
	S14-6/1	184.39
	S14-8/26	223.38
SEDIMENT	(B/01)-11/5	192.15
	(B/6)-11/5	114.55
	(B/08)-11/5	660.21
	(B/10)-11/5	146.32
	(B/11)-11/5	331.74
	(B/13)-11/5	258.13

APPENDIX D

HEAVY METAL ANALYSIS

Table D1. Results of heavy metal analysis in soils and sediments

ND: Not Detected
Units are in mg/kg

	Site	Fe	Mn	As	Co	Cr	Cu	Ni	Pb	Zn
SURFACE SOIL	S(2)-6/1	5.13	0.26	6.91	5.93	33.13	14.91	28.12	18.99	65.16
	S(2)-8/26	4.03	0.19	3.97	2.54	40.45	10.37	25.49	14.76	49.08
	S(5)-6/1	7.56	0.49	11.30	7.85	23.22	11.30	24.26	15.96	44.46
	S(5)-8/26	5.13	0.35	6.62	3.70	27.23	8.84	22.41	15.56	38.07
	S(6)-6/1	0.63	0.01	1.49	ND	8.52	2.69	7.22	6.52	14.47
	S(6)-8/26	1.13	0.03	2.01	ND	21.92	3.54	12.17	8.31	19.24
	S(9)-6/1	2.63	0.12	3.12	ND	37.99	15.33	18.36	14.32	42.26
	S(9)-8/26	3.57	0.17	4.93	0.81	37.48	9.43	18.62	14.28	53.14
	S(10)-6/1	2.73	0.11	4.05	0.99	26.37	11.49	18.66	15.33	49.88
	S(10)-8/26	2.75	0.12	3.68	0.10	22.66	7.28	17.20	13.39	43.17
	S(11)-6/1	3.33	0.13	4.81	1.83	32.84	9.70	24.61	15.60	48.85
	S(11)-8/26	3.64	0.14	4.99	2.49	30.39	12.57	19.61	26.09	62.60
	S(13)-6/1	4.36	0.23	5.79	2.59	39.28	14.80	27.22	17.24	64.44
	S(13)-8/26	3.94	0.22	6.03	1.34	40.63	15.15	34.28	15.99	66.29
	S(14)-6/1	2.10	0.09	3.37	ND	21.42	6.55	17.06	13.01	37.45
	S(14)-8/26	1.31	0.05	1.08	ND	18.21	4.69	11.43	21.73	50.27
6" DEEP SOIL	S(2)-6/1	7.36	0.44	9.77	11.06	28.61	19.33	42.28	22.18	80.78
	S(2)-8/26	7.97	0.50	11.94	13.34	38.46	19.37	45.94	22.39	82.61
	S(9)-6/1	3.78	0.16	4.33	2.38	38.12	9.19	20.38	13.76	53.47
	S(9)-8/26	4.01	0.18	5.33	1.78	45.33	11.68	18.09	15.04	55.39
	S(11)-6/1	4.00	0.16	5.39	4.30	36.07	11.86	23.01	17.21	60.18
	S(11)-8/26	4.40	0.20	4.91	2.55	39.85	12.09	26.68	20.16	65.16
	S(14)-6/1	2.34	0.09	2.71	ND	29.72	6.41	18.43	12.40	33.21
	S(14)-8/26	2.29	0.08	3.05	ND	24.46	7.06	23.42	12.60	35.24
SEDIMENT	W(1)-11/5	3.33	0.03	3.12	3.45	55.42	17.15	22.45	19.35	58.42
	W(6)-11/5	0.88	0.02	1.62	ND	22.11	3.05	8.05	8.08	17.79
	W(8)-11/5	4.98	0.07	3.33	8.71	60.13	17.52	25.77	17.90	76.15
	W(10)-11/5	1.23	0.02	2.33	ND	23.56	5.43	11.03	10.02	28.68
	W(11)-11/5	2.65	0.05	2.39	ND	39.12	11.18	16.92	16.50	55.43
	W(13)-11/5	2.00	0.04	2.95	ND	29.26	7.91	14.28	13.04	42.04

APPENDIX E

STATISTICAL ANALYSIS

Table E1. Correlation output

Turbidity and Total Suspended Solids

Summary of Fit

RSquare	0.568209
RSquare Adj	0.562294
Root Mean Square Error	2.754437
Mean of Response	5.922667
Observations (or Sum Wgts)	75

Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	1	728.8238	728.824	96.0632
Error	73	553.8452	7.587	**Prob > F**
C. Total	74	1282.6691		<.0001*

Parameter Estimates

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	-0.070393	0.689236	-0.10	0.9189
DO	0.5993619	0.061152	9.80	<.0001*

DO and Temperature

Summary of Fit

RSquare	0.003596
RSquare Adj	-0.01005
Root Mean Square Error	5.262335
Mean of Response	9.999067
Observations (or Sum Wgts)	75

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	7.2953	7.2953	0.2634
Error	73	2021.5283	27.6922	**Prob > F**
C. Total	74	2028.8236		0.6093

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	9.1360103	1.787916	5.11	<.0001*
Temp	0.0436834	0.085108	0.51	0.6093

DO and BOD

Summary of Fit

RSquare	0.568209
RSquare Adj	0.562294
Root Mean Square Error	2.754437
Mean of Response	5.922667
Observations (or Sum Wgts)	75

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	728.8238	728.824	96.0632
Error	73	553.8452	7.587	**Prob > F**
C. Total	74	1282.6691		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-0.070393	0.689236	-0.10	0.9189
DO	0.5993619	0.061152	9.80	<.0001*

E. coli and Rainfall

Summary of Fit

RSquare	0.5065
RSquare Adj	0.4360
Root Mean Square Error	13.9697
Mean of Response	21.4444
Observations (or Sum Wgts)	9

Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	1	1402.1445	1402.14	7.1848
Error	7	1366.0777	195.15	**Prob > F**
C. Total	8	2768.2222		0.0315

Parameter Estimates

Term	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	-23.7354	17.4867	-1.36	0.2168
DO	14.1138	5.2654	2.68	0.0315

Table E2. T-test for inlet (W1) & outlet (W2)

DO

Test-Stat	**W1 (Inlet)**	**W8 (Outlet)**
Mean	4.923	11.567
Variance	13.72097	23.137
Observations	8	8
Pearson Correlation	0.460	
Hypothesized Mean Difference	0	
df	7	
t Stat	-4.156	
P(T<=t) one-tail	0.002	
t Critical one-tail	1.894	
P(T<=t) two-tail	0.004	
t Critical two-tail	2.364	

Chloride

Test-Stat	**W1 (Inlet)**	**W8 (Outlet)**
Mean	21.631	9.290
Variance	155.542	2.189
Observations	9.000	9.000
Pearson Correlation	0.520	
Hypothesized Mean Difference	0.000	
df	8.000	
t Stat	3.146	
P(T<=t) one-tail	0.007	
t Critical one-tail	1.860	
P(T<=t) two-tail	0.014	
t Critical two-tail	2.306	

Sulfate

Test-Stat	**W1 (Inlet)**	**W8 (Outlet)**
Mean	11.280	4.326
Variance	138.900	6.421
Observations	9.000	9.000
Pearson Correlation	0.464	
Hypothesized Mean Difference	0.000	
df	8.000	
t Stat	1.924	
P(T<=t) one-tail	0.045	
t Critical one-tail	1.860	
P(T<=t) two-tail	0.091	
t Critical two-tail	2.306	

Ammonia

Test-Stat	**W1 (Inlet)**	**W8 (Outlet)**
Mean	0.307	0.106
Variance	0.112	0.009
Observations	7.000	7.000
Pearson Correlation	0.244	
Hypothesized Mean Difference	0.000	
df	6.000	
t Stat	1.642	
P(T<=t) one-tail	0.076	
t Critical one-tail	1.943	
P(T<=t) two-tail	0.152	
t Critical two-tail	2.447	

Phosphorus

Test-Stat	**W1 (Inlet)**	**W8 (Outlet)**
Mean	478.778	266.778
Variance	234899.194	13176.944
Observations	9.000	9.000
Pearson Correlation	0.373	
Hypothesized Mean Difference	0.000	
df	8.000	
t Stat	1.399	
P(T<=t) one-tail	0.100	
t Critical one-tail	1.860	
P(T<=t) two-tail	0.199	
t Critical two-tail	2.306	

Table E3. ANOVA

Phosphorus (water)

Summary of Fit

Rsquare	0.090913
Adj Rsquare	0.066671
Root Mean Square Error	341.6415
Mean of Response	418.1336
Observations (or Sum Wgts)	78

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Column 2	2	875435.8	437718	3.7502	0.0280
Error	75	8753918.0	116719		
C. Total	77	9629353.8			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Early summer	27	459.222	65.749	328.24	590.20
Late summer	24	263.065	69.737	124.14	401.99
Mid-summer	27	514.884	65.749	383.91	645.86

Heavy metals

Iron

Summary of Fit

Rsquare	0.141534
Adj Rsquare	0.077944
Root Mean Square Error	1.799832
Mean of Response	3.506333
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Column 11	2	14.41998	7.20999	2.2257	0.1274
Error	27	87.46371	3.23940		
C. Total	29	101.88370			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	4.51875	0.63634	3.2131	5.8244
Sediment	6	2.51167	0.73478	1.0040	4.0193
Surface soil	16	3.37313	0.44996	2.4499	4.2964

Std Error uses a pooled estimate of error variance

Manganese

Summary of Fit

Rsquare	0.238205
Adj Rsquare	0.181776
Root Mean Square Error	0.121802
Mean of Response	0.158333
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Column 11	2	0.12525208	0.062626	4.2213	0.0254
Error	27	0.40056458	0.014836		
C. Total	29	0.52581667			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	0.226250	0.04306	0.1379	0.31461
Sediment	6	0.038333	0.04973	-0.0637	0.14036
Surface soil	16	0.169375	0.03045	0.1069	0.23185

Std Error uses a pooled estimate of error variance

Arsenic

Summary of Fit

Rsquare	0.182896
Adj Rsquare	0.122369
Root Mean Square Error	2.493353
Mean of Response	4.577333
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	37.57137	18.7857	3.0218	0.0654
Error	27	167.85381	6.2168		
C. Total	29	205.42519			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	5.92875	0.8815	4.1200	7.7375
Sediment	6	2.62333	1.0179	0.5348	4.7119
Surface soil	16	4.63438	0.6233	3.3554	5.9134

Std Error uses a pooled estimate of error variance

Cobalt

Summary of Fit

Rsquare	0.197902
Adj Rsquare	0.09764
Root Mean Square Error	3.471672
Mean of Response	4.091579
Observations (or Sum Wgts)	19

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	47.57955	23.7898	1.9738	0.1713
Error	16	192.84010	12.0525		
C. Total	18	240.41965			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	6	5.90167	1.4173	2.8971	8.906
Sediment	2	6.08000	2.4548	0.8760	11.284
Surface soil	11	2.74273	1.0467	0.5237	4.962

Std Error uses a pooled estimate of error variance

Chromium

Summary of Fit

Rsquare	0.136058
Adj Rsquare	0.072062
Root Mean Square Error	10.45187
Mean of Response	32.39867
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	464.5059	232.253	2.1260	0.1388
Error	27	2949.5255	109.242		
C. Total	29	3414.0313			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	35.0775	3.6953	27.495	42.660
Sediment	6	38.2667	4.2670	29.512	47.022
Surface soil	16	28.8588	2.6130	23.497	34.220

Std Error uses a pooled estimate of error variance

Copper

Summary of Fit

Rsquare	0.04144
Adj Rsquare	-0.02956
Root Mean Square Error	4.754829
Mean of Response	10.59567
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	26.38982	13.1949	0.5836	0.5648
Error	27	610.42672	22.6084		
C. Total	29	636.81654			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	12.1238	1.6811	8.6744	15.573
Sediment	6	10.3733	1.9412	6.3904	14.356
Surface soil	16	9.9150	1.1887	7.4760	12.354

Std Error uses a pooled estimate of error variance

Nickel

Summary of Fit

Rsquare	0.200244
Adj Rsquare	0.141003
Root Mean Square Error	8.074681
Mean of Response	21.44833
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	440.7756	220.388	3.3802	0.0490
Error	27	1760.4128	65.200		
C. Total	29	2201.1884			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	27.2788	2.8548	21.421	33.136
Sediment	6	16.4167	3.2965	9.653	23.180
Surface soil	16	20.4200	2.0187	16.278	24.562

Std Error uses a pooled estimate of error variance

Lead

Summary of Fit

Rsquare	0.049683
Adj Rsquare	-0.02071
Root Mean Square Error	4.453675
Mean of Response	15.59033
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	27.99856	13.9993	0.7058	0.5026
Error	27	535.55093	19.8352		
C. Total	29	563.54950			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	16.9675	1.5746	13.737	20.198
Sediment	6	14.1483	1.8182	10.418	17.879
Surface soil	16	15.4425	1.1134	13.158	17.727

Std Error uses a pooled estimate of error variance

Zinc

Summary of Fit

Rsquare	0.089703
Adj Rsquare	0.022274
Root Mean Square Error	17.16927
Mean of Response	49.77933
Observations (or Sum Wgts)	30

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Category	2	784.3175	392.159	1.3303	0.2812
Error	27	7959.1599	294.784		
C. Total	29	8743.4774			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
6" deep soil	8	58.2550	6.0703	45.800	70.710
Sediment	6	46.4183	7.0093	32.036	60.800
Surface soil	16	46.8019	4.2923	37.995	55.609

Std Error uses a pooled estimate of error variance

APPENDIX F

DETERMINATION OF TOTAL PHOSPHORUS

Persulfate Digestion

Requirements

Chemicals/Equipment/Supplies

1. Phenolphthalein indicator solution
2. Sulfuric acid solution, H_2SO_4
3. Ammonium persulfate, $(NH_4)_2S_2O_8$ or potassium persulfate, $K_2S_2O_8$
4. 1 N NaOH
5. Standard phosphate solution
6. Autoclave
7. Volumetric flasks (50 ml, 100 ml, 250 ml, 500 ml, 1000 ml)
8. Erlenmeyer flasks (250 ml)
9. Drying oven
10. Weighing machine
11. Desiccator
12. Centrifuge machine
13. Centrifuge tubes (50 ml)*
    (*required during sediment analysis)
14. Aluminum foil
15. Acid bath
16. Pipette (5 ml, 10 ml, 50 ml)

Preparation of reagents and standard solutions

1. Acid Bath

Any form of strong acids such as nitric acid, sulfuric acid or hydrochloric acid can be used to prepare acid bath. 20-50% acid solution is prepared in a polypropylene (or any other acid proof) container. The main purpose of this acid bath is to remove hard stains and chemicals from the glassware. After acid bath wash, the glassware should be rinsed with DI-water.

2. Phenolphthalein indicator solution

Dissolve 80 mg phenolphthalein in 100 ml methanol.

3. Standard phosphate solution (Stock solution)

Dissolve 219.5 mg anhydrous KH_2PO_4 in DI-water and dilute up to 1000 ml. This gives: *1 ml stock solution = 50 µg* PO_4^{3-}*P*. Depending on the expected range of phosphorus in the samples, required range of standard solutions should be prepared using the stock solution.

4. 1 N NaOH

Dissolve 40 gm NaOH in 1000 ml DI-water.

5. Sulfuric acid solution

Add 300 ml of conc. H_2SO_4 to approximately 600 ml DI-water and dilute to 1000 ml with DI-water. (Make sure that acid should be added to water, not water to conc. Acid)

Methods

In Persulfate Digestion method, the main objective is to convert all of the phosphorus, including organic phosphorus, to orthophosphate. This is then measured in a colorimetric assay.

1. The required range of standard solutions should be prepared depending on the expected range of phosphorus in the samples. In this study, for water samples, the following concentrations of standard were prepared: 0, 10, 25, 50, 75, 100, and 125 µg P. For sediment samples, the following concentrations were prepared: 0, 50, 100, 250, 500, 750, and 1000 µg P.

2. For water samples, add 50 ml of these to Erlenmeyer flasks using 50 ml volumetric flasks. For sediment samples, these should be dried in an oven first at 105° C for 24 hours. After drying, add 1.5 g of dry samples and 50 ml of DI-water to Erlenmeyer flasks. Then add 1 ml sulfuric acid solution and 0.4 g ammonium persulfate, $(NH_4)_2S_2O_8$ or potassium persulfate, $K_2S_2O_8$.

3. Cover the flasks with aluminum foil and autoclave for 30 minutes.

4. For water samples, when flasks are cool, add 1 drop phenolphthalein indicator solution and neutralize to a faint pink color with NaOH. Then transfer to 100 ml volumetric flasks and bring up to 100 ml with DI-water.

5. For sediment samples, when flasks are cool, empty the contents (sediment + water) into 50 ml centrifuge tube and centrifuge for 10-15 minutes. Using pipettes, transfer supernatant to 100 ml volumetric flasks. After that, these samples are similarly neutralized as given in Step-4.

Ascorbic Acid Method

Requirements

Chemicals/Equipment/Supplies

1. Spectrophotometer
2. Disposable cuvettes
3. Volumetric flasks (50 ml)
4. 4 N Sulfuric acid, H_2SO_4
5. Potassium antimony tartrate, $K(SbO)C_4H_4O_6.2H_2O$
6. Ammonium molybdate solution, $(NH_4)_6Mo_7O_{24}.4H_2O$
7. Ascrobic acid
8. Murphy-Riley mixed reagent

Preparation of reagents

1. 4 N Sulfuric acid, H_2SO_4

Add 112 ml conc. H_2SO_4 in 1000 ml DI-water to get 4 N H_2SO_4.

2. Potassium antimony tartrate solution

Dissolve 2.2 g $K(SbO)C_4H_4O_6.2H_2O$ in 400 ml DI-water in a 500 ml volumetric flask, and bring up to 500 ml with DI-water. Store the solution at 4°C.

3. Ammonium molybdate solution
Dissolve 20 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 ml DI-water

4. Murphy-Riley mixed reagent

Mix 125 ml 4 N H_2SO_4, 12.5 ml $K(SbO)C_4H_4O_6.2H_2O$, 37.5 $(NH_4)_6Mo_7O_24.4H_2O$, 1.06 g ascorbic acid in 250 ml DI-water. This solution is stable only for 4 hours. The final solution has light greenish yellow color. If the color of the solution is green or blue, there is contamination. Prepare the mixture again in clean flask. If the contamination persists, there could be contamination in either of the solution prepared.

Methods

In Ascorbic Assay method, the main objective is to react the phosphate in the digested samples with Murphy-Riley mixed reagent to form a colored compound (molybdenum blue). This is then measured with a spectrophotometer.

1. Turn on the spectrophotometer at least 30 minutes prior to use to allow the lamp to warm up. Set the wavelength to 880 nm.

2. Mix 40 ml of the water samples from persulfate digestion with 10 ml mixed reagent in 50 ml volumetric flasks. For sediment samples, mix 5 ml solution from persulfate digestion with 35 ml DI-water and 10 ml mixed reagent in 50 ml volumetric flasks. React at room temperature for 10-30 minutes.

3. The phosphate standards should also be treated similarly as mentioned in Step-2 while analyzing for both water and sediment samples.

4. First, zero the spectrophotometer at 880 nm with a 0 µg PO_4^{3-}P. Then, take absorbance values for standards from spectrophotometer at 880 nm at least after 10 minutes (but do not wait longer than 30 minutes). Prepare a standard curve in an excel spreadsheet by plotting between phosphate concentration and absorbance to get linear regression curve.

5. Determine the phosphorus concentration in the samples by using the standard curve equation to convert absorbance to phosphate. Determine concentration by dividing by the sample volume. Report the concentration as µg P/L.

(Derived from Clesceri et al., 2005)

APPENDIX G

LETTER OF PERMIT

SPECIAL USE REQUEST
BLACK HAWK COUNTY CONSERVATION BOARD

AREA

Black Hawk____ Hickory Hills____ McFarlane____

Other Area : Beaver Valley Wetland

Activity Permitted: Research study on the critical role of wetlands in maintaining ecosystem balance.

Limitations and Conditions: Area must be entered by foot. All vehicles must remain in parking lot. Main vehicle will be a Chevy Colorado Official Iowa plate 10345. Research team may access any part of the wetland. Primary people on site; Sushil Tuladhar and Dr. Mohammad Z. Iqbal.
Entrance to the area is restricted during pelican migration

Date: April 15, 2011 to August 15, 2011

Hours: 8am – 6pm

Organization/Group/Club: University of Northern Iowa, Earth Science Department

Person Responsible: Sushil Tuladhar

Address: 219 E. Street

City: Cedar Falls **State: Iowa** **Zip: 50613**

Phone # H= 319-273-2998 **W=**

AUTHORIZED BY: Mike Hendrickson; North Unit Ranger; 319-269-4155
DATE March 29, 2011

DATE FAXED OR GIVEN TO RANGER:_____

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