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Temporal dynamics of nutrient flux across hydrologic unit boundaries

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TEMPORAL DYNAMICS OF NUTRIENT FLUX ACROSS HYDROLOGIC UNIT BOUNDARIES

An Abstract of a Thesis
Submitted
in partial Fulfillment
of the Requirements for the Degree
Master of Science

Md. Aminul Haque
University of Northern Iowa
December 2013

ABSTRACT

The study was done in Dry Run Creek watershed, a small sub-urban watershed in the northwestern part of Black Hawk County, Iowa. Different hydrologic units like, wetland, agricultural area, urban area, and stream channels were compared in terms of nutrient transport. Soil, surface water, and groundwater samples were collected from May, 2012 to October, 2012. Among the hydrologic units, agricultural land has the highest organic matter percentages, infiltration rate, soil nitrate, and total phosphorus. High infiltration rate and amount of nutrients in agricultural soil made those areas more vulnerable to vertical infiltration of pollutants. Agricultural and urban soils had similar organic matter percentages. A constructed wetland in the study area is actively recycling nutrients from its surface water. Stream bank soil has low nitrate and phosphorus but high chloride compared to other units. In general nitrate and total phosphorus concentrations are high during the months of agricultural activities (May-July), indicating active influx from agricultural lands. Urban areas contribute significant amount of phosphorus and total suspended sediment into the stream. Spatial and temporal variations of nutrients in soil and water indicate active recycling of nutrients within the watershed and their interactions with other hydrologic units. Nutrient distribution in soil at different depth profiles indicates active vertical movement of nutrients. Though agricultural soil has high nitrate compared to urban areas, groundwater from urban areas shows high dissolved nitrate compared to agricultural areas. Total nitrate-N, phosphorus, and TSS load leaving the watershed in three months (June-August) was calculated as $2.5\text{x}10^5$ kg, 594 kg, and $2.2\text{x}10^5$ kg respectively. During the study period precipitation was very low and the year

was unusually dry. Repetition of the study in a year of greater rainfall will give valuable information regarding the consistency of the results and effects of dry weather in nutrient transport.

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This Study by: Md. Aminul Haque

Entitled: TEMPORAL DYNAMICS OF NUTRIENT FLUX ACROSS HYDROLOGIC UNIT BOUNDARIES

has been approved as meeting the thesis requirement for the

Degree of Master of Science in Environmental Science.

Date Dr. Mohammad Z. Iqbal, Chair, Thesis Committee

Date Dr. Maureen E. Clayton, Thesis Committee Member

Date Dr. James C. Walters, Thesis Committee Member

Date Dr. Michael J. Licari, Dean, Graduate College

Dedicated to my parents

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INTRODUCTION

Background

“This is the prospect from the watershed, and when the traveler reaches it, it is a good thing to take an hour's leisure and lookout on the visible portions of the journey, since never in one's life can one see the same view twice.” From Stark (2013), page 169.

Historically we know about human influence on water quality. In present days, watersheds are heavily impacted by human activities. During the beginning of human civilization people were not aware of the fact that their activities can affect their environment. However, with the increase of population, knowledge and technology now we know that our activities do heavily influence the environment. Increasing human population increases food demand with stress being put on the use of water resources. Use of fertilizers is routinely increasing to meet the growing food demand. Lands are routinely converted to urban areas to accommodate the growing population. These factors eventually influence the hydrology and water quality of a watershed. In general, land use practices change various hydrologic processes like evapotranspiration, interception, infiltration, and surface runoff (Dunne and Leopold, 1978). As these processes control nutrient transport, land use practices have direct impact on nutrient distribution in a watershed. Hydrologic processes of a watershed are very dynamic, but it is worth examining a snapshot of these processes.

A drop of water that starts its journey from a small watershed eventually ends up in the ocean. However, as water is the universal solvent, while travelling it dissolves and carries nutrients, pollutants, and suspended solids from one point to another. Water with dissolved substances passes through different hydrologic units and each hydrologic unit plays specific roles to transport, store or dissolve these substances. Complete understanding of the bigger picture requires detailed knowledge of every component of the system. Similarly, to understand hydrologic processes it is important to know how different hydrologic units interact within a watershed. This study was conducted to understand the dynamics of nutrients in different hydrologic units in and around the Cedar Falls area.

Suspended sediments, nutrients and pesticides are the major pollutants associated with agriculture and urban activities (Osmond et al., 1995; Carpenter et al., 1998). Nutrients like nitrogen (N) and phosphorous (P) cause eutrophication in surface water bodies (Carpenter et al., 1998). One of the biggest examples of eutrophication is “Gulf of Mexico Hypoxia”. It is observed around the northern Gulf of Mexico to the west of the Mississippi and Atchafalaya River deltas (USGS, 2013 a). The largest hypoxic zone in Gulf of Mexico was observed in mid-summer 2002 with an aerial extent of 22,000 km^2 and the lowest areal extent was observed in 1988 which was 40 km^2 (LUMCON, 2013). Average areal extend was 8,000-9,000 km^2 in 1985-1992 but average areal extend increased above 15,000 km^2 in 1993-2001 (Rabalais et al., 2002). In 2013, expected areal extend of hypoxic zone in July is more than 22,000 km^2 (LUMCON, 2013). In recent years hypoxic zones have increased and become newly introduced in many coastal areas. Decrease in dissolved oxygen concentration in coastal areas is the most rapidly changed environmental variable. This change has been heavily influenced by human activities (Diaz, 2001; Rabalais et al., 2007).

Paleoenvironmental study showed that Gulf of Mexico hypoxia is not a natural feature. Increase of this hypoxic zone was positively correlated with population growth, urbanization and use of fertilizers in the fields (Rabalais et al., 2007). Nutrients and organic matter coming from the Mississippi and the Atchafalaya River discharge were the main causes behind this hypoxic zone. Land use change like deforestation and conversion of wetlands and prairies to agricultural land in last 50 years have dramatically changed the ability of the ecosystem to transform nutrients (Rabalais et al., 2007). The main source of nitrate and phosphorus in the Mississippi and the Atchafalaya River is fertilizers. In between 1981 to 1985 about 44% of nitrogen and 28% of phosphorus applied as fertilizers in the fields in the Mississippi and the Atchafalaya River basin was delivered to the Gulf of Mexico (Turner and Rabalais, 1991). Primary source of these nutrients is the Upper Mississippi River basin which includes the Cedar River (Goolsby et al., 1999). On an average river basins of Minnesota, Iowa, Illinois, and Ohio delivered nitrogen load from 1,500 to more than 31,000 kg N km^{-2} each year from 1980 to1996. This number is much higher compared to the surrounding areas. Annual average total N yields were 2,450, 2,290, 2,202, 3,090 and 1,850 kg N km^{-2} yr^{-1} in the Cedar, Iowa, Skunk, Raccoon, and Des Moines River basins in Iowa, respectively. Primary source of this nitrogen is agricultural fertilizers (Goolsby et al., 2001). During the last century, nitrate concentration in the Mississippi River basin has increased dramatically, in most cases by a factor of 2 to 5. Basins that have high row crops or high population density showed the highest nitrate concentration. During 1980-1996, the Gulf of Mexico received 1,568,000 tons total N annually, of which 61% was in the form of nitrate (Goolsby et al., 2001).

Iowa rivers, situated in the heart of the U.S Corn Belt contribute a major portion of the nitrate-nitrogen load to the Mississippi River basin (Goolsby et al., 1999). The total input ranges from $2.04\text{x}10^8$ to $2.22\text{x}10^8$ kg annually, which is about 25% of the nitrate delivered by the Mississippi River to the Gulf of Mexico (Libra, 1998). Eastern Iowa Rivers like the Cedar River, Iowa River and Wapsipinicon River contribute the major portion of the nutrients delivered by Iowa Rivers. In the year 1996, the amount was $7.9\text{x}10^7$ kg of total nitrogen and $6.8\text{x}10^6$ kg of total phosphorus from these three major eastern Iowa watersheds (Becher et al., 2000). A study by Tavener and Iqbal (2003) showed that in summer 2000 (months of July, August, and September) the Cedar River watershed contributed about $2.99\text{x}10^6$ kg total nitrogen and $2.39\text{x}10^5$ kg total phosphorus to the Mississippi River basin. The Dry Run Creek watershed is also contributing nutrients through the Cedar River and the Mississippi River all the way to the Gulf of Mexico.

Hydrologic Units

The terms watershed and hydrologic unit can be used to mean the same thing. All watersheds include one or more hydrologic units but all hydrologic units can’t be defined as a watershed (VDCR, 2013). Watershed is defined as “a unit of natural or disturbed land on which all the water that falls collects by gravity and fails to evaporate and runs off via a common outlet (Black, 1996, page 140)”. It plays a big part in the hydrologic cycle and is one of the basic units of water supply. The definition of a watershed can be extended to include manmade structures like parking lots, roof tops, and artificial drainage ways. On the other hand, hydrologic units can connect watersheds and are sometimes defined as specific areas within a watershed. Hydrologic units not only collect water within the boundary of it but also from outside its boundary (VDCR, 2013). According to Poehls and Smith (2011, page 160) a hydrologic unit is "an area representing a distinct feature of a water-bearing, water-producing, or water-transmitting entity" such as an aquifer, a soil zone, a lake, or a reservoir. Hydrologic units as described here are not the same as federal standard hydrologic units which represent regions or sub-regions. Hydrologic units in this study represent small units within the watershed, such as prairie, agricultural land, urban area, wetland, and streams. Among these units, prairie is free from any anthropogenic activities and it does not have any major outside nutrient sources. Thus the prairie was taken as a control to compare nutrient concentrations in other hydrologic units. This comparison helped to visualize the impact of human activities in other hydrologic units concerning nutrient dynamics.

Prairie

Prairies are considered as temperate grasslands. Usually it has moderate to low precipitation with flat or rolling terrain (Environmental Encyclopedia, 2011a). It is also known as North American grasslands, which are historically extended throughout the North America but disappeared during the nineteenth and the twentieth centuries due to agricultural settlement (Environmental Encyclopedia, 2011a). Dominant vegetation in prairies is grasses, herbs, and shrubs. There are mainly three groups of prairies in North

America, namely wet, mesic, and dry. They are also generally characterized by tallgrass prairie, mixed, or shortgrass prairie, depending on the quality of soil and rainfall (Prairie Frontier, 2013). In wet prairie, the soil is usually very moist most of the growing season and has poor water drainage. The average precipitation amount in wet prairie is 10- 30 inches a year (Prairie Frontier, 2013). Mesic prairie has good drainage and fertile soil. These prairies are suitable for agricultural usage. As most of these kinds of prairies have been converted to agricultural land it is one of the rare types of prairie (Prairie Frontier, 2013). Dry prairies usually have wet to very dry soil as they have good drainage. Often, these prairies can be found on uplands or slopes (Environmental Encyclopedia, 2011a; Prairie Frontier, 2013).

Agricultural Land

"Agriculture can be defined as the systematic and controlled use of living organisms and the environment to improve the human condition. 'Agricultural land' is the land base upon which agriculture is practiced" (PALC, 2013). Agricultural lands are mainly used to produce agricultural products. These lands can be divided into arable land, permanent crops, and permanent pasture (FAOSTAT, 2013). Arable lands are used for temporary purposes like growing cereals, cotton, potatoes and other vegetables for specific amount of time in a year. Temporally unused lands are also included in this category but lands abandoned due to shift of cultivation are not included (FAOSTAT, 2013). Permanent crops refer to long time use of a land, like fruit plantation. Permanent pastures are Meadows and pastures, used for grazing of livestock. Altogether, arable land and land in permanent crops are named as cultivable land. Agricultural land could be irrigated or non-irrigated land based on the use of artificial irrigation (FAOSTAT, 2013). In the Dry Run Creek watershed, most of the lands are cultivable and non-irrigated lands.

Urban Area

The U.S. Census Bureau (2010) defines an urban area as: "Core census block groups or blocks that have a population density of at least 1,000 people per square mile (386 per square kilometer) with surrounding census blocks that have an overall density of at least 500 people per square mile (193 per square kilometer)". Cedar Falls is a city in Black Hawk County, Iowa, United States with a population of 39,260 (U.S. Census Bureau, 2010). Out of 29.61 square miles (76.69 km^2) of total area, the city has 28.75 square miles (74.46 km^2) of land and 0.86 square miles (2.23 km^2) of water (U.S. Census Bureau, 2010). Cedar Falls is situated in the North-East part of the Dry Run Creek Watershed and it occupies about 20% of the watershed area (Iowa DNR, 2002).

Wetland

Wetlands can be identified by their soil, vegetation, and hydrology (Water Encyclopedia, 2013 a). Wetlands cannot exist without water. In wetlands water is the main factor in defining the nature of soil development and the kinds of plant and animal groups that exist in the soil and on its surface (U.S. EPA, 2013 a). Specifically, a wetland is an area that is intermittently or always saturated or covered by surface water or groundwater that shows hydric soils (unique soils associated with extended saturation) and that characteristically supports or is capable of supporting hydrophytic (water-loving) vegetation (U.S. EPA, 2013 a). Wetlands are very unique ecosystems that support a large variety of organisms. Wetlands receive high amount of materials by surface runoff and accumulation of decaying plants. These materials from different sources have high nutrient content which is available for different species of plants, organisms and animals (U.S. EPA, 2013 a). These nutrients and water make wetlands a perfect habitat for fish, amphibians, and insects. Wetlands are the only home for one-third of threatened and endangered species in the United States and about half of them stay in wetlands at least some part of their lives (U.S. EPA, 2013 a). The wetland in this study is a constructed wetland and also acts as flood water retention basin.

Stream

Water from rain, snow melt, or other sources flow from up gradient to down gradient. When the ground surface receives an excess amount of flowing water which can’t be used up by plants, infiltrate into the ground, or evaporated into the air, stream is created (Water Encyclopedia, 2013 b). Whatever the source, the stream always joints rivulets from other low spots and follows the lowest places in the landscape. Joining of rivulets in down gradient makes large streams which eventually create different drainage patterns. The type of drainage pattern depends on soil type, geomorphology, gradients and vegetation patterns. Streams run through other hydrologic units and most of the pollutants and nutrients leave the watershed by stream water (Water Encyclopedia, 2013 b). In this study, Dry Run Creek watershed has dendritic drainage pattern and it runs through agricultural area, urban area, and wetland.

Nutrients

Nutrients are essential chemicals for plants and animals to live, grow, and produce energy. Plants and animals collect nutrients in different forms from the surrounding environments (Environmental Encyclopedia, 2011b). No plant or animal can survive without the essential nutrients as they are the key elements to regulate body processes. Nutrients needed in large amount are called macronutrients like nitrogen, phosphorus, calcium, sulfur, and magnesium. Nutrients needed in minute amounts are called micronutrients or trace elements like cobalt, iron and sodium (Environmental Encyclopedia, 2011b). This study will primarily focus on nitrogen and phosphorus.

Nitrogen

Nitrogen is the major component of the earth's atmosphere. About 78 percent of atmosphere is nitrogen. It has an atomic number of seven and an atomic weight of fourteen. Nitrogen is more soluble in air compared to water and atmosphere has about 200 times more nitrogen compared to ocean (Environmental Encyclopedia, 2011c). Despite its easy availability, most organisms can't use it directly due to its very stable triple bond. Some bacteria fix atmospheric nitrogen to bioavailable forms like nitrate, ammonia, and amino acids. Most plants use these forms of nitrogen (Environmental Encyclopedia, 2011c). Nitrogen cycle (Figure 1) shows how nitrogen moves through many forms.

Nitrogen (N) can be organic or inorganic and is present in surface water in both dissolved and particulate forms. Plants can uptake only the inorganic forms which are a breakdown product of organic nitrogen by different natural processes. The most common inorganic forms of nitrogen are ammonium (NH_4^+) and nitrate (NO_3^-). Ammonium ion (NH_4^+) can be stored in the soil whereas nitrate (NO_3^-) and nitrite (NO_2^-) are not bound to soil. Nitrate from soil can get into the groundwater and from there it can be transformed

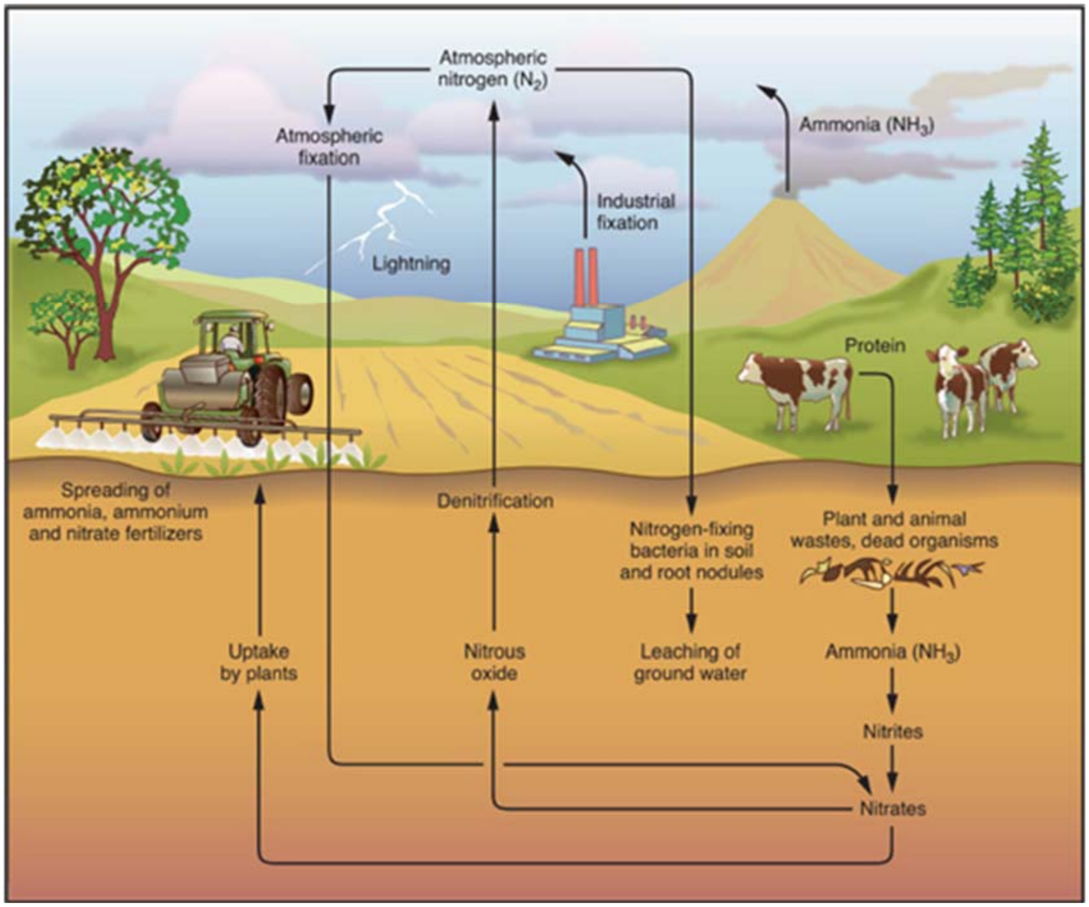


Figure 1. Nitrogen cycle (Environmental Encyclopedia, 2011c).

into nitrogen (N_2, NO or N_2O) and ammonia (NH_3) gases by biological activities. These gases can escape out of the soil or be released into the Earth's atmosphere (Environmental Encyclopedia, 2011c).

Common sources of nitrate in surface water are municipal sewage, atmospheric deposition, biological N fixation, soil organic N, and/or nitrogen in fertilizers. In Iowa, agriculture is the primary nonpoint source for surface water nitrate, especially from anhydrous ammonia fertilizers (Goolsby et al., 1999). Fertilizers, septic systems, and manure storage are the main source of nitrate in groundwater (Schilling et al., 2007;

Steinheimer et al., 1998). Nitrogen applied as fertilizer in the field often is not taken up fully by plants, volatilized, or carried away by surface runoff. Excess nitrogen thus leaches to the groundwater as nitrate. Thus, nitrogen applied in the field makes the nitrogen available to crops and also can elevate the concentration in groundwater. In Iowa stream, nitrate is mainly coming from base flow and tile drainage (Goolsby et al., 1999; Schilling et al., 2007).

Eutrophication is the biggest environmental concern due to high nutrients like nitrate on freshwater bodies. Nitrate is used by bacteria and other organisms and stimulates the growth of phytoplankton. When phytoplankton dies, they are decomposed in a process that consumes oxygen to form CO_2. This causes hypoxic zones (LUMCON, 2013). High nitrate intake is also harmful for humans, especially for infants. It has health effects like methemoglobinemia. The maximum contaminant level (MCL) of nitrate-nitrogen in drinking water is 10 mg/L (U.S. EPA, 2013 b).

Phosphorus

Phosphorus (P), is an important macronutrient with atomic number 15 and atomic weight 30.97. Like nitrogen, it is needed for plant growth and function and one of the three major components of agricultural fertilizers (Environmental Encyclopedia, 2011d). Depending on the environment, P can be the main reason and also the limiting nutrient for eutrophication in mainland surface water bodies (MPCA, 2007). Phosphorus can’t volatilize into atmosphere due to the lack of a gaseous form. Both particulate and dissolved forms are common for phosphorus in water (Figure 2). Dissolved forms can be organic and inorganic. In aerobic surface water bodies most phosphorus is found in the

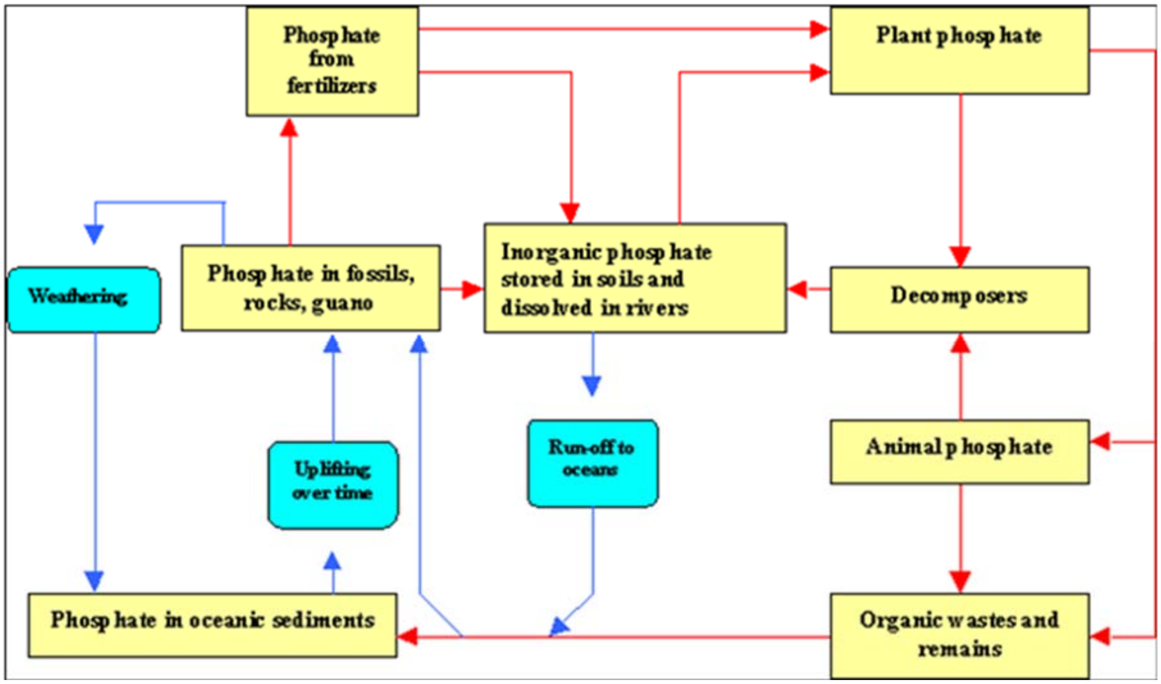


Figure 2. Phosphorus cycle (Lenntech Phosphorus Cycle, 2004).

particulate phase adsorbed onto sediment particles like silt and clay. Among inorganic forms orthophosphates are the most common in water. Main sources of orthophosphate are natural weathering and solution of mineral, soil erosion and transport, and soil fertilizers (MPCA, 2007).

Phosphorus from fertilizers or other sources can reach surface water bodies as dissolved in water and/or attached to soil particles. Soil erosion and surface runoff carry the soil particles with phosphorus to surface water bodies. As phosphorus is mainly transported adsorbed to soil particles it is less mobile compared to nitrogen (MPCA, 2007). Thus the possibility of phosphorus to get into the groundwater is low. Phosphorus is also less soluble in water compared to nitrogen. For these reasons, phosphorus accumulates in lakes or stream beds. Bottom sediments in lakes or stream also receive phosphorus from decaying plants. Adsorbed in bottom sediments, phosphorus can act as long term source for nutrients and cause eutrophication (Iqbal et al., 2006; MPCA, 2007). Figure 3 shows how nitrogen and phosphorus reach surface water from agricultural fields.

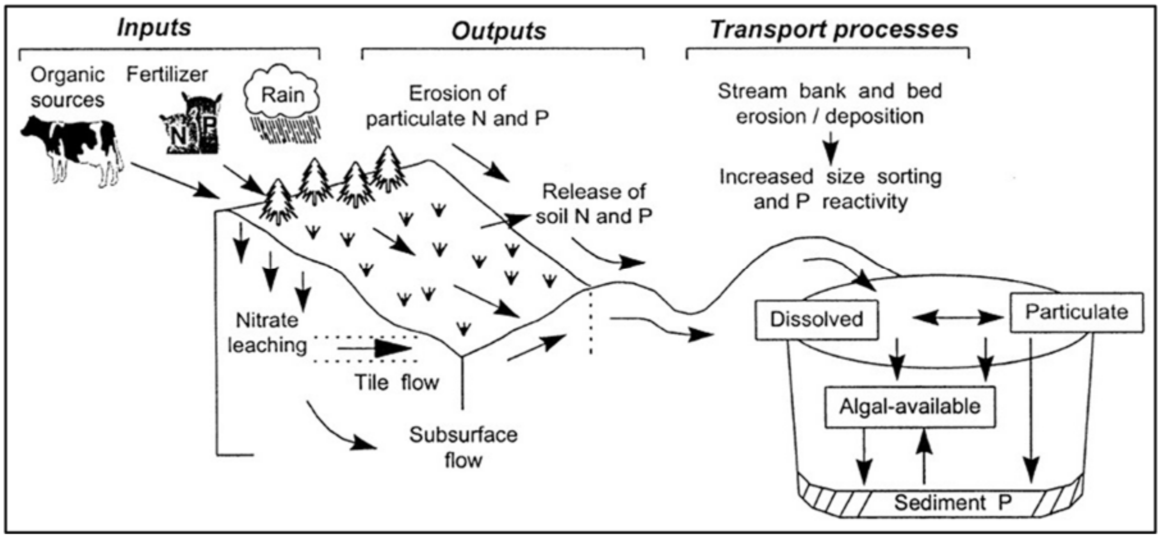


Figure 3. Inputs, outputs and processes of transport of P and N from agricultural land (Carpenter et al., 1998).

<u>Suspended Sediments</u>

According to U.S. EPA (2013 c) suspended and bedded sediments are “particulate organic and inorganic matter that suspend in or are carried by the water, and/or accumulate in a loose, unconsolidated form on the bottom of natural water bodies”. Particles as suspended sediments prevent penetration of the sunlight into the water. Lack of sunlight has direct impact on stream physical habitat and on stream biota like submerged aquatic vegetation (SAV) (U.S. EPA, 2013 c).

Suspended sediment is one of the major causes for impaired surface water bodies in the United States (U.S. EPA, 2002) and also for Midwestern streams (Iowa DNR, 2004). Surface runoff, stream erosion, and stream bank erosion, timber harvesting, construction, and landslides produce suspended sediments. Hydrologic parameters like precipitation, infiltration rate and discharge also control suspended sediments (U.S. EPA,2013 c). Agricultural activities like row crop production and pasture contribute about 38% and 25% of suspended sediment to U.S. streams (Welsch, 1991). Burwell et al. (1977) showed that most soil erosion and nutrient loss occur in the first two months of agricultural activities. In Iowa about 70% of the land is used for either raw crops or pasture. Surface runoff is the dominant process to generate suspended sediments in these practices (Burkart et al., 1994). Besides, rapid urbanization is found to be a major contributor of suspended sediments to the surface water runoff due to landslides, channel-bank erosion, and road surface erosion (Nelson and Booth, 2002).

Previous Study

Agricultural leachates that accumulate in the field and aquifers contribute nitrate to streams by way of base flow and surface runoff (Iqbal, 2002). In the Corn Belt, Iowa uses the highest amount of nitrogen fertilizers. In Iowa, the major sources of nitrate in groundwater are leachates from nitrogen fertilizers and manures applied in the agricultural fields (Spalding and Exner, 1993). In last few decades, use of nitrogen fertilizers had increased dramatically, especially in Corn Belt. Many studies found this as the biggest threat to groundwater nitrate contamination. These studies also showed that shallow groundwater nitrate concentration had exceeded drinking water MCL of 45 ppm due to agricultural activities (U.S. EPA, 1986). Chemical fertilizers and manure are also proven as sources of nitrate in groundwater by isotopic studies. These studies showed that nitrogen transport to the water table depends on soil characteristics, recharge mechanism, and rate of fertilizer application (Randall and Mulla, 2001). A study conducted by Gautam and Iqbal (2010) using nitrogen isotope showed mixed origin of groundwater nitrate in Iowa. According to this study groundwater nitrate came from both nitrogen fertilizers and soil organic nitrogen.

Iowa's surface water has among the highest nitrate and phosphorus concentration in the US surface water bodies; average stream nitrate-N concentration was 11 ppm and that in groundwater was 5.1 ppm Kalkhoff et al., (2000). In one study Iqbal (1996) found that 41% of the wells tested in the basin exceeded the MCL of nitrate (45 mg/L as NO_3^-) set by EPA (U.S. Environmental Protection Agency) for drinking water standard. Another study found that nine drinking water wells in Cedar River basin exceeded MCL for nitrate (Iqbal, 2000).

A water budget study with oxygen isotope tracer was conducted by Iqbal (2002) in the Cedar River basin of northeastern Iowa in 2000. It showed that 83% of stream discharge was coming from pre-storm water with 17% from rain events. Pressure created in the aquifer due to precipitation discharged 36% of the total recharge to the aquifer into the stream. Schilling (2005) study showed nitrate primarily delivered to stream by base flow and tile drainage. Row crop production has increased the base flow and tile drainage in Iowa. An increase of 13-52% row crop production had increased base flow by 7-31%

in several Iowa Rivers during 1940-2000. This eventually increased nitrate concentration in surface water bodies by two to three fold. As nitrate is delivered to Iowa streams mainly by base flow and tile drainage, increased base flow and tile drainage means more nitrate in surface water (Schilling and Zhang, 2004). A similar relationship was observed in Walnut Creek and Squaw Creek in Iowa (Schilling and Spooner, 2006).

According to Kalkhoff et al. (2000), nitrates are more common in agricultural areas compared to urban areas. Moreover, agricultural areas with row crop production and livestock feeding are the most affected areas. Kalkhoff et al. (2000) found nitrates in shallow aquifer in 94% of the agricultural areas whereas it was 71% of the urban areas. The Nitrate-N MCL was exceeded in 39% of the samples from agricultural areas but none from urban areas. Land use practices are a good predictor of stream pollution. Several studies showed the relationship of land use practices with nitrogen and phosphorus pollution in streams and shallow groundwater. In many studies, nitrogen and phosphorus concentrations were positively correlated with agricultural practices (Coulter, et al., 2004; Jordan et al., 1997; Osborne and Wiley, 1998; Schilling and Libra, 2000). Medium sized basins with intensive row crops production and animal feeding operations had the highest occurrences of nitrates (Kalkhoff et al., 2000). Schilling and Libra (2000) studied 25 different watersheds in Iowa and found positive correlation between concentrations of nitrate and percentages of row corps.

Figure 4 shows the trends and magnitudes of major nitrogen sources in the Mississippi-Atchafalaya River Basin (MARB). These sources vary widely in small basins. The fertilizer curve showed dramatic regional increase of fertilizer use since the

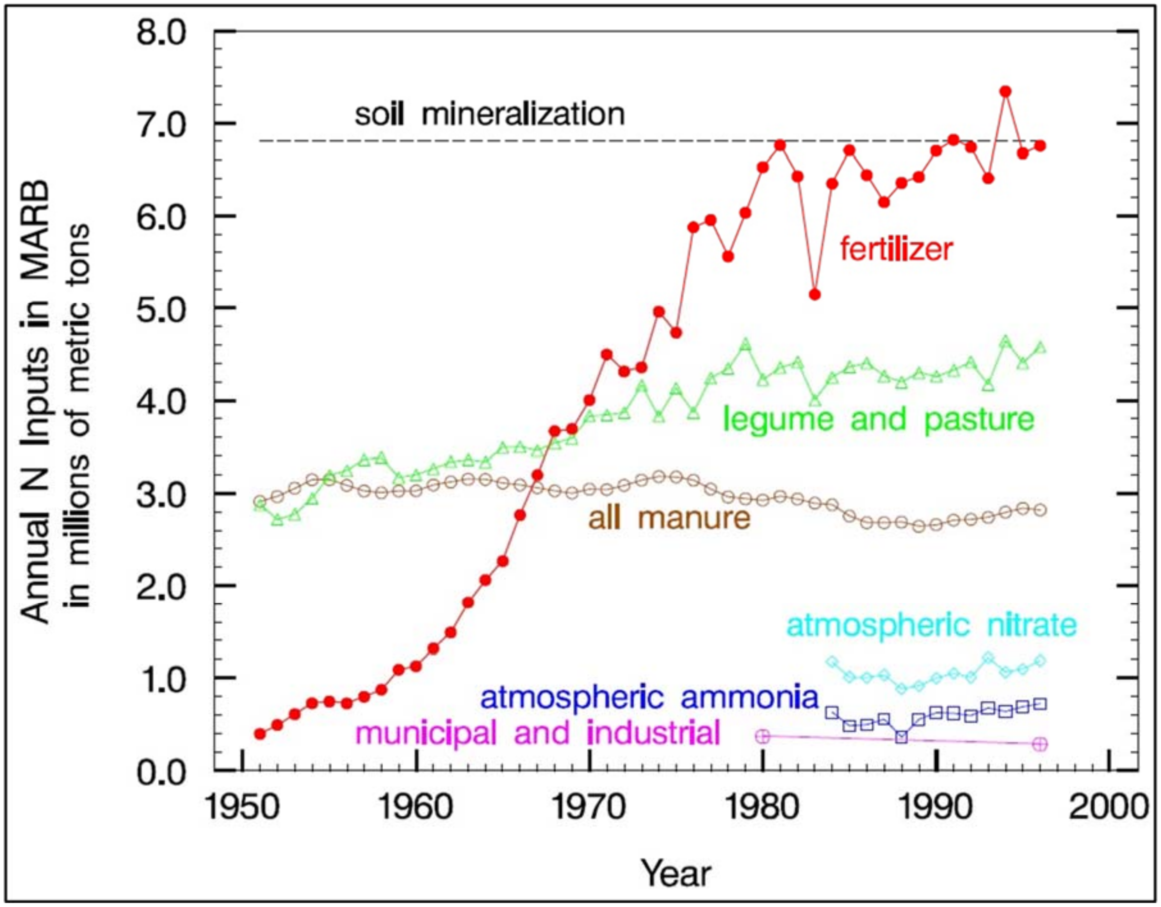


Figure 4. Annual nitrogen inputs to the Mississippi-Atchafalaya River Basin (Goolsby et al. 1999).

middle of 20th century. Though fertilizers and manure are the primary source of nitrogen, decay of soil organic matter and plant residues can also contribute significant amount of nitrogen in water or soil (Goolsby et al. 1999; Paul 1997). But it is difficult to quantify the contribution from different sources. Leguminous crops like alfalfa, soybeans, and peanuts that effectively fix atmospheric nitrogen to soil can contribute a significant amount of nitrogen to agricultural recharge (Figure 4).

About 10-50% of applied nitrogen fertilizers can get into the groundwater from heavily fertilized well drained fields (Böhlke and Denver, 1995). Nitrate levels in streams and wells have been correlated positively with regional and local increase of nitrogen fertilizer use by long term studies. A positive correlation has been found between nitrate concentration in shallow ground water and thickness of unsaturated zone, drainage, and recharge rate (Hallberg and Keeney, 1993).

Shallow water table conditions and poor drainage can promote denitrification or reduce nitrification during recharge (Nolan, 2001). Usually deep aquifers are protected by layers of shale and clay but shallow alluvial aquifers don't have this kind of protection. As a result shallow aquifers are easy to pollute by available nitrate in the surface. On the other hand, longer flow path, adsorption, degradation, and dispersion reduce the amount of nitrate in deep aquifer. Thus a decreasing trend of nitrate concentration with depth was observed in alluvial aquifers (Kalkhoff et al., 2000**)**.

The correlation of high nitrate in groundwater to agricultural lands is known since the 1970s. A variety of nitrogen sources in agricultural soils could be converted to nitrate and incorporated in ground water recharge (Keeney and Olson, 1986). A study in southeastern Iowa by Steinheimer et al. (1998) showed the effect of long term use of fertilizers on groundwater nitrate distribution. The study reveals that it takes about 40-100 months for a parcel of saturated groundwater to reach a stream section from the most remote area of a watershed. Sometimes it can take several years for dissolved nitrate to reach the surface water via subsurface flow. This study reported negligible contribution of nitrate from other sources and confirmed that nitrogen fertilizers are the major sources of nitrate in groundwater in Iowa.

Top soil erosion causes suspended sediments, decreases light penetration in streams and transports nutrients from agricultural fields. A five year study in Missouri Valley by Burwell et al. (1977) showed that phosphorus mainly enters the water by soil erosion as it forms complex compounds with soil cations like calcium, iron and aluminum. Robertson and Nash (2008) found that major transportation of phosphorus from agricultural fields to streams occurs via P being adsorbed to soil particles. Phosphorus and nitrogen can be transported through suspended sediments and deposited in lakes or other water bodies. Lake sediments containing phosphorus and nitrate can be a continuous source of nutrient and cause eutrophication (Iqbal el al., 2006; Iqbal and Fields, 2009).

Suspended sediment supply varies largely throughout the year and also with precipitation. This makes accurate field measurements very complicated. Accurate and continuous measurements of suspended sediments is very time consuming and expensive. Wide variation of suspended solids in response to precipitation, especially in smaller streams, makes it a more complex situation. Scientists have developed numerous estimations and methods to overcome these difficulties and have an accurate measure of suspended sediment in streams. A study done by Phillips et al. (1999) to find out the most accurate method of estimating sediment loads showed that bigger watershed size reduces the accuracy of the data. Accuracy also depends on sampling frequency; the more frequent samples the more accurate data.

Hypothesis and Objectives

The Federal Clean Water Act requires all states to develop lists of impaired water bodies that are not meeting water quality standard (WQS) for designated uses. This list of impaired water bodies is referred to as the state's 303(d) list. The Dry Run Creek watershed was declared an impaired watershed in 2002, which means it failed to maintain the water quality of desired uses. The two major causes of pollution in this watershed are excessive bed load sediments and surface runoff from rapidly urbanized areas (Iowa DNR, 2011). Previous study showed that this watershed is also contributing a significant amount of nutrients to the Cedar River (Shrestha, 2008). The main source of these nutrients is fertilizers used in agricultural lands. Nutrients are generally transported through surface runoff and as base flow (Shrestha, 2008).

The hypothesis of this project is that different hydrologic units like streams, wetlands, agricultural land, urban areas, and prairies have different roles in transporting nutrients within the watershed. Different parts of the watershed will respond differently for different nutrients or pollutants. Better understanding of these units and their responses to contain nutrients or pollutants will give a better picture about the nutrient processes.

This study was conducted to assess the differences between these hydrologic units and to understand their roles in nutrient transport. Soil, surface water, and groundwater samples were taken from different hydrologic units over a six month period to visualize a complete scenario. The key objectives of this study were to investigate the following:

- Nutrient flux between the urban and the agricultural sections of the watershed.

- Distribution of nutrients in different hydrologic units.
- Temporal dynamics of nutrients across hydrologic unit boundaries.
- Spatial dynamics of nutrients across hydrologic unit boundaries.
- Differences between an undisturbed hydrologic unit (prairie) and units with measurable activities.
- Function of a constructed wetland within a watershed.
- Nutrient budget within the watershed.
- Conceptual model of nutrient cycling within the watershed.

Water quality improvement plans require knowledge of different hydrologic units within the watershed as well as their functions and roles for nutrient transport. If we know the response of different parts of the watershed to a particular element it will help to organize and customize watershed management plans. Besides, understanding the functions of each hydrologic unit and their roles will help to develop site specific management plans.

CHAPTER 2

STUDY AREA

The study area of this research consists of Dry Run Creek (DRC) and Cedar Hills Sand Prairie (CHSP) in Cedar Falls and surrounding areas. The Dry Run Creek watershed and the Cedar Hills Sand Prairie are both located in Black Hawk County, Iowa (Figure 5).

Dry Run Creek Watershed

The Dry Run Creek watershed is a small sub-urban watershed. Located in the northwestern part of Black Hawk County, Iowa (Figure 5). It is also part of Iowan Surface ecoregion (Iowa DNR, 2011). The study area is a part of the Cedar River watershed (Figure 6), which drains into the larger Mississippi River as Iowa River near the Quad city area in southeast Iowa (Figure 7).

Small first order streams in the Dry Run Creek watershed originate from mostly agricultural areas and travel down to the Cedar Falls metropolitan area before entering the Cedar River northeast of town (Figure 8). This is a third order watershed with dendritic drainage pattern. The total stream length is over 50 miles with 22 miles of main channel draining about 61.05 km^2 (35 mi^2) surface area (Iowa DNR, 2011). This makes DRC a very important water course for the area. Close monitoring of this water body is expected to give valuable data. As DRC runs over urban and agricultural lands (Figure 8) its water quality reflects the area activities that are responsible for the existing chemical characteristics of the watershed.

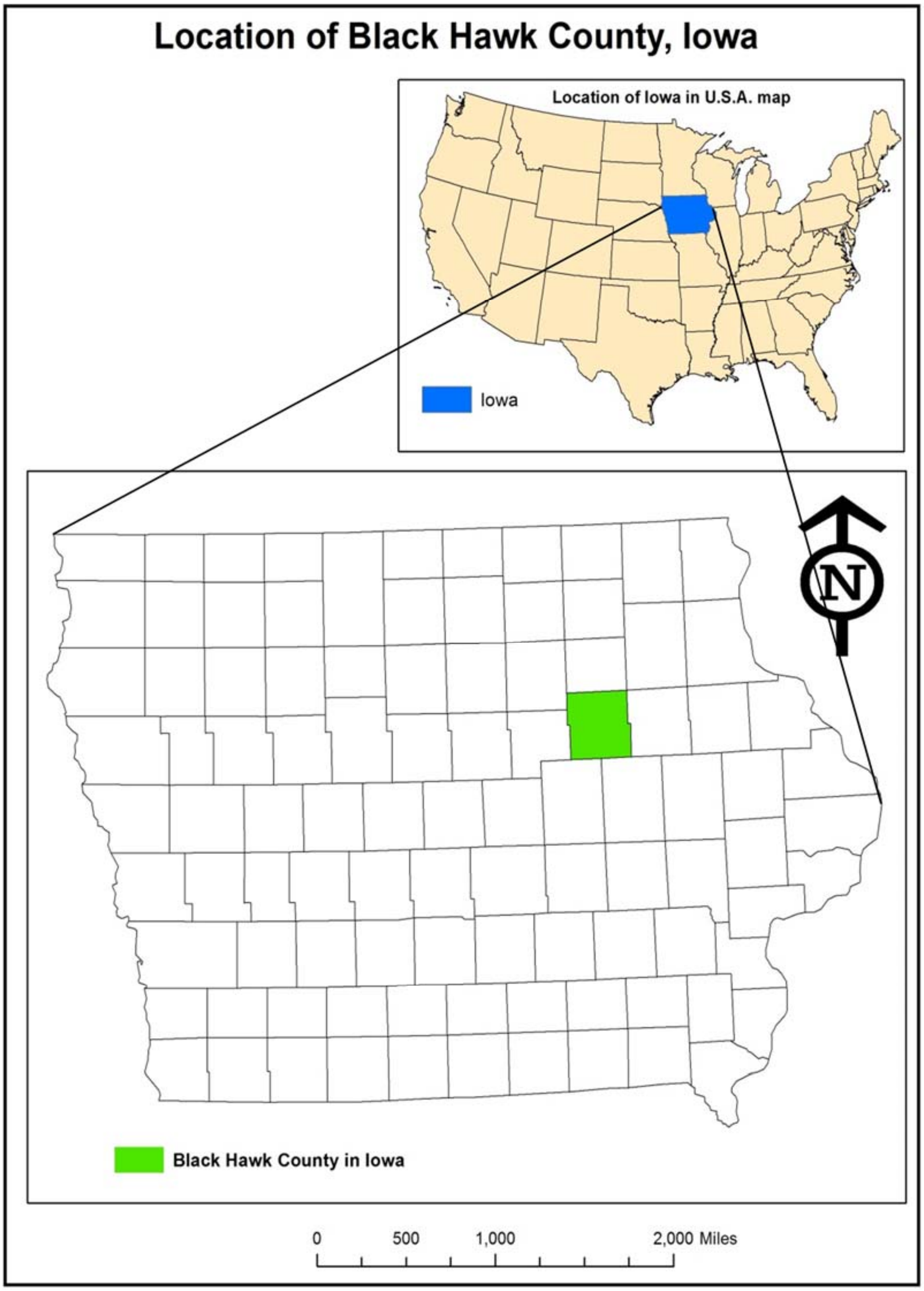


Figure 5. Location of Black Hawk County, Iowa.

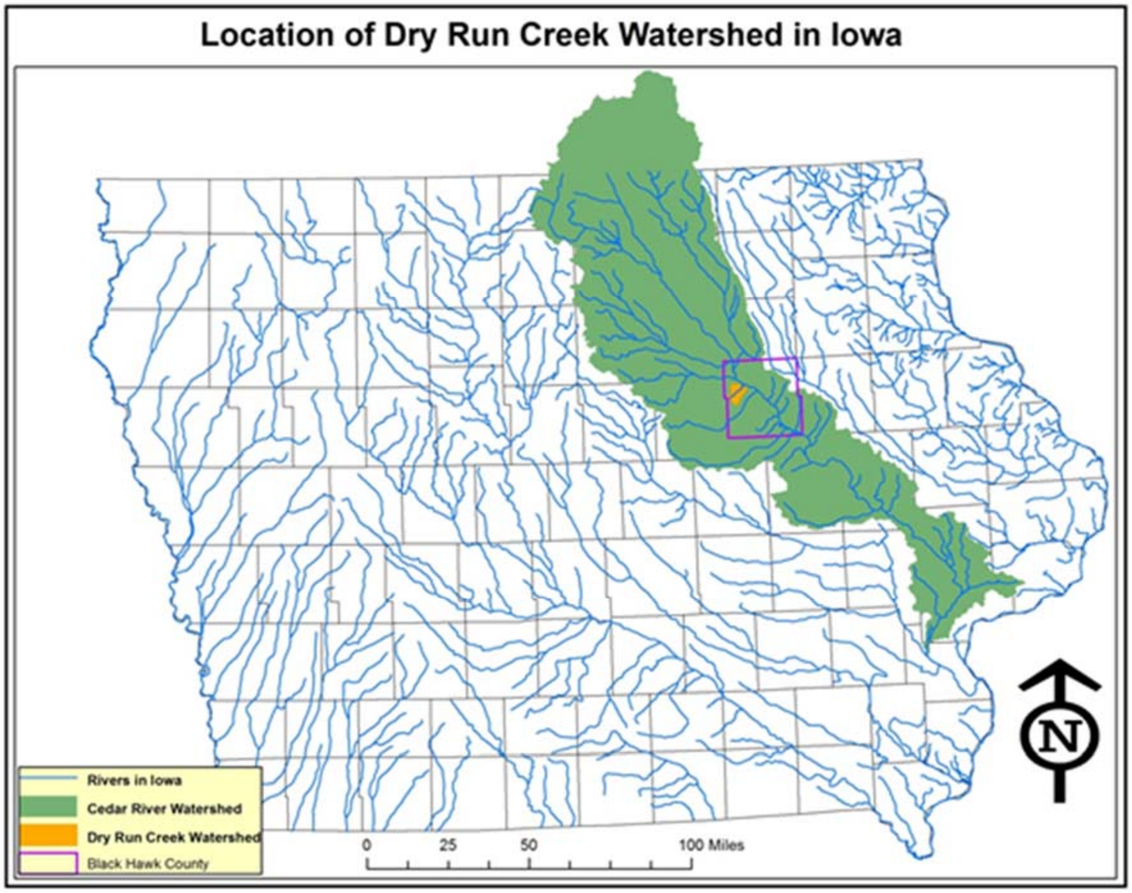


Figure 6. Location of Dry Run Creek watershed in Iowa.

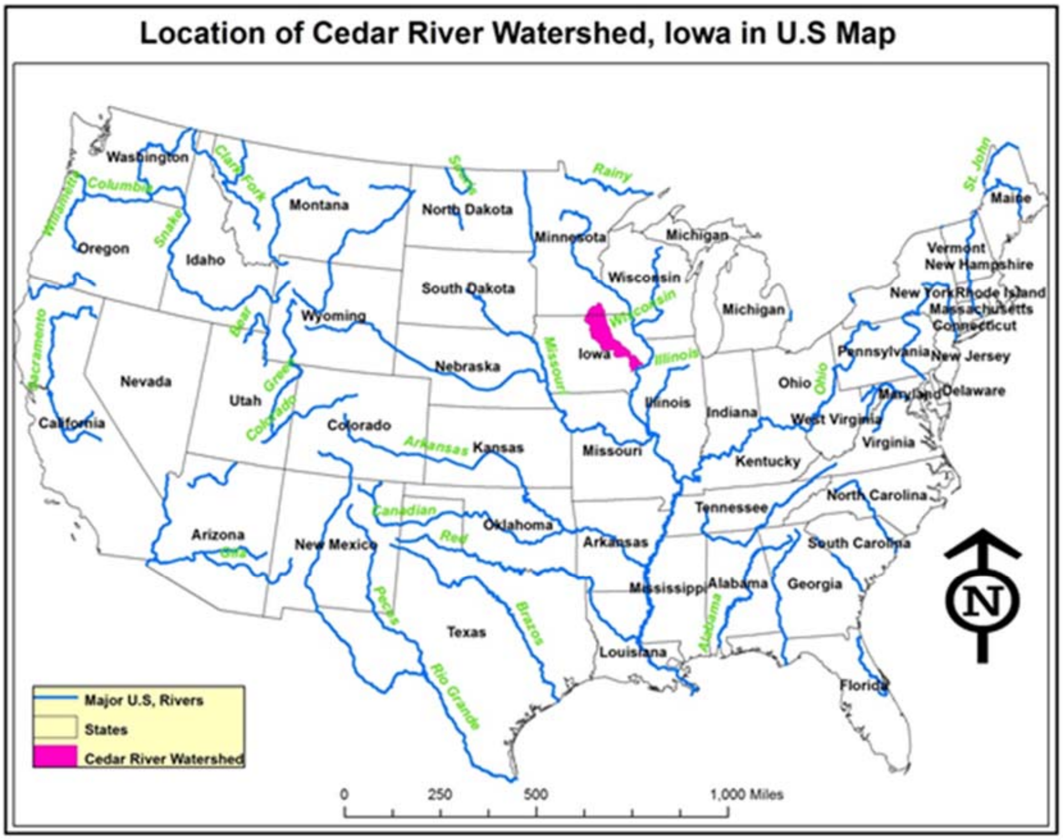


Figure 7. Location of Cedar River watershed.

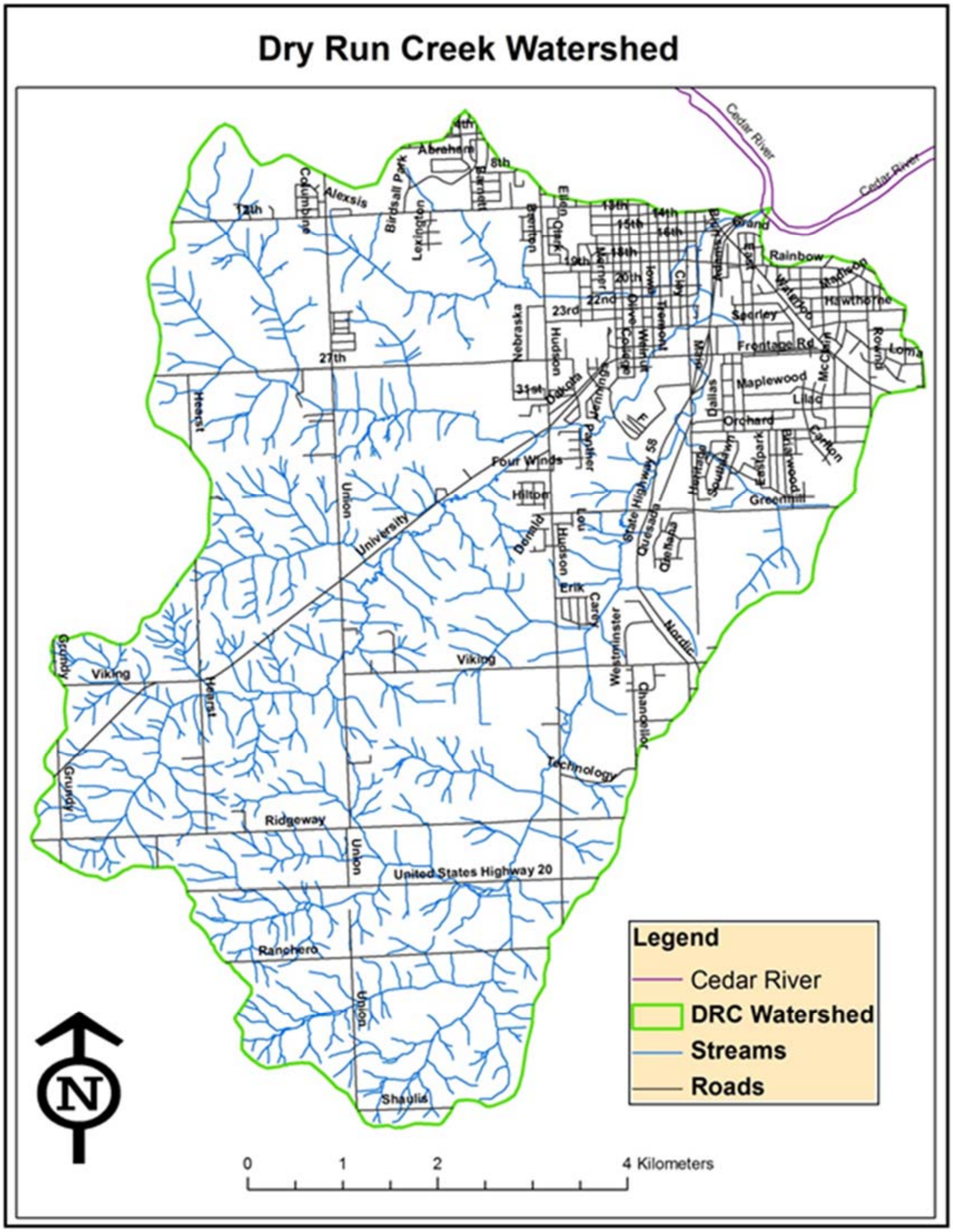


Figure 8. Dry Run Creek (DRC) watershed.

Cedar Hills Sand Prairie

Cedar Hills Sand Prairie (Figure 9 and 10) is about 90 acres in area containing a sand prairie, sedge meadow, and a small fen. It is located ten miles northwest of Cedar Falls in western Black Hawk County (Nature Conservancy, 2013).

The Cedar Hills Sand Prairie was discovered in 1969. At that time it was known as 'Mark Sand Prairie' and was maintained by University of Northern Iowa Biological Preserves. The land was purchased by the Iowa chapter of The Nature Conservancy in 1985 (Iowa DNR, 2013).

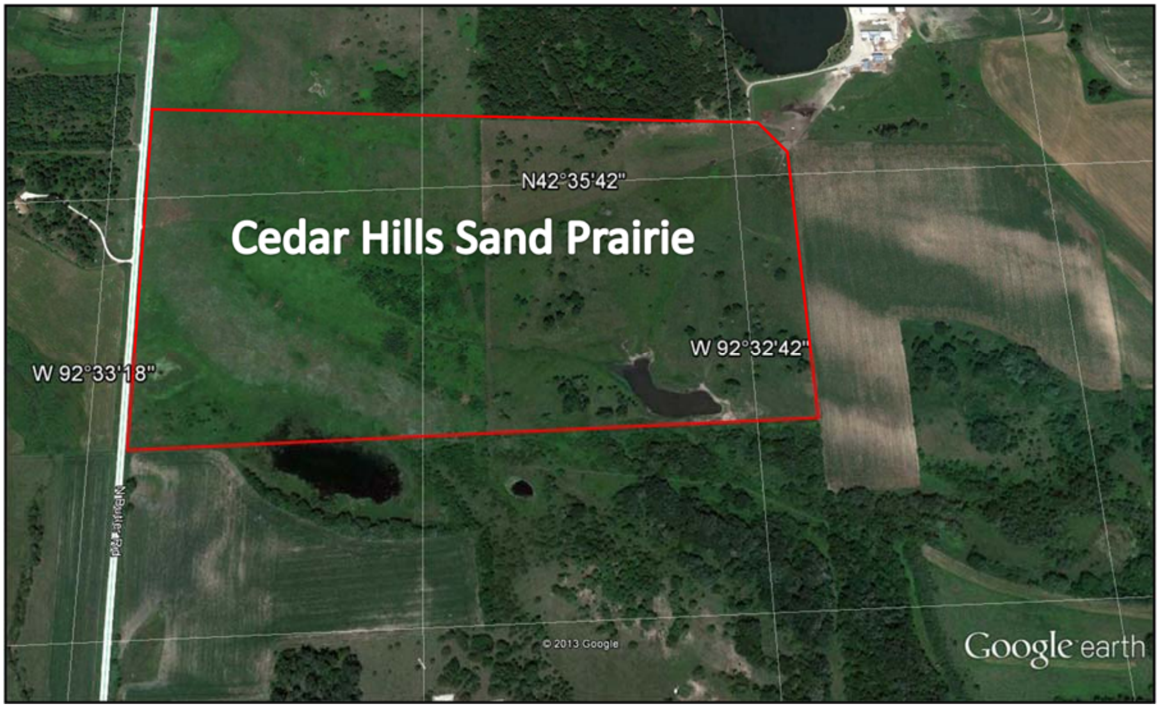


Figure 9. Aerial view of Cedar Hills Sand Prairie.

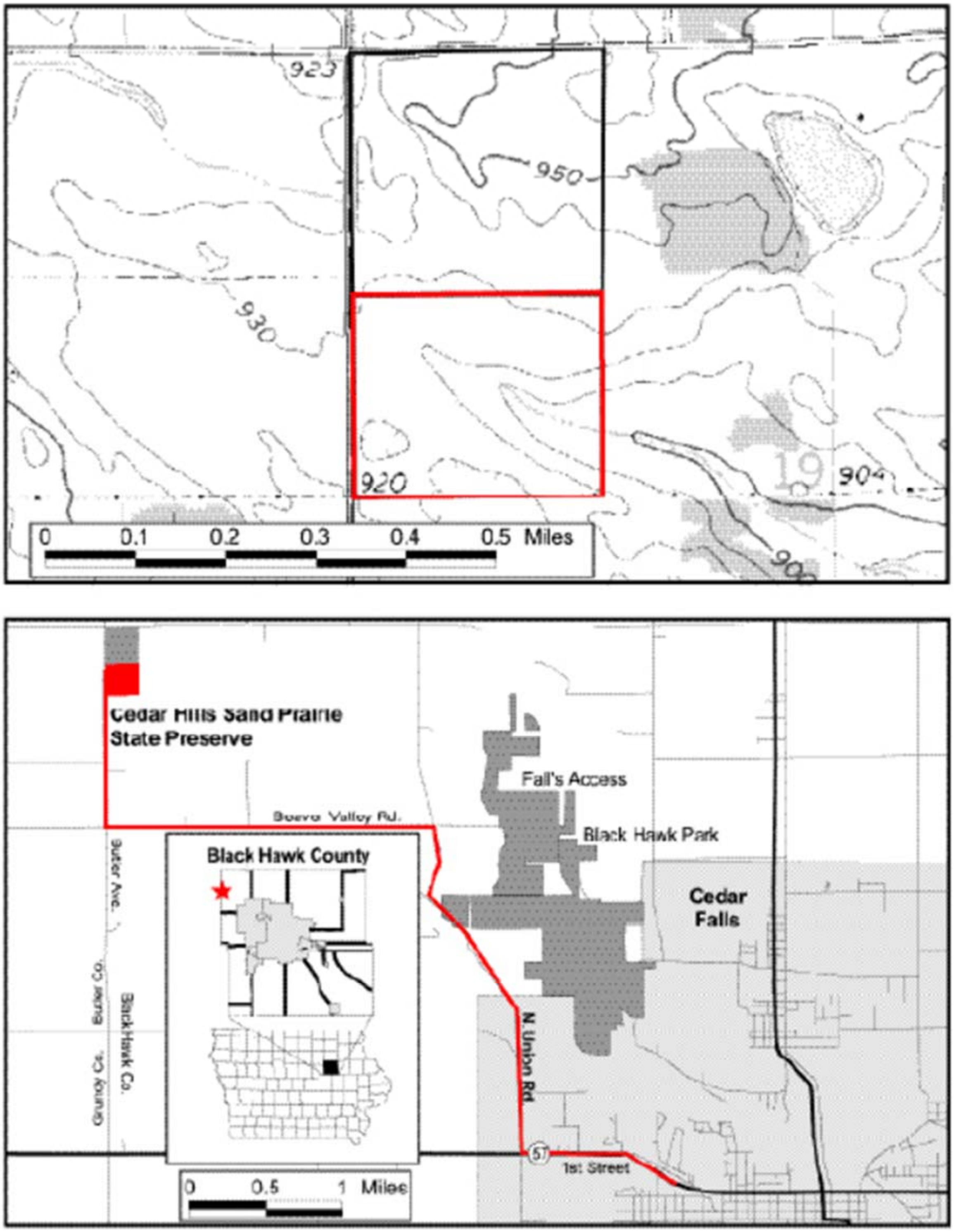


Figure 10. Map view of Cedar Hills Sand Prairie (Iowa DNR, 2013).

The prairie supports a large variety of plants and animals, including more than 360 species of native plants, 107 species of diatoms, 50 species of bird and butterflies and more than 90 species of leafhoppers (Nature Conservancy, 2013) (Figure 11). Within this prairie area there are few marshes in the southern part that occupy depressions and store water, and also a small fen. Sediments of this area are primarily sand, admixed with silt and clay. Prairies are situated in the upland parts of a drainage basin and these are the first places from where water starts its journey to rivers. Prairies are free from any kind of anthropogenic activities so they represent an ideal condition of the natural environment. Sand prairies in Iowa formed by aeolian sand deposition from adjacent river valleys about 4000 years B.P. and it is located in the Iowan Surface landform region (Emerman et al., 2002).

Watershed Hydrogeology

The shallow alluvial aquifer system formed by the ancient Cedar River channels is the most easily accessed aquifer in the area. This aquifer system is made up of highly permeable gravel, sand and silt deposits derived from glacial deposits or bedrock erosion (Olcott, 1992). The age of this aquifer system is Holocene and the thickness range is 30 to 100 feet. This aquifer system has interceded silt and clay layers with permeable sand and gravel layers (Wahl et al., 1978). This aquifer system primarily receives recharge from surface infiltration through overlying shallow alluvial sediment layer. It also receives water from influent streams. The water table of this system ranges from 5 to 20 feet (Olcott, 1992). This shallow aquifer system is more susceptible to any kind of surficial contamination like agricultural and/or industrial pollution as it doesn’t have any

Figure 11. Landform and vegetation in Cedar Hills Sand Prairie.

continuous confining layer and shallow water table (Hoyer and Hallberg, 1991). Below the surface alluvial system there is bedrock aquifer system. This aquifer consists of sedimentary rock layers like limestone and dolomite as well as siltstone and clay. These materials were deposited about 75 million to 550 million years ago when the area was occupied by ancient seas, rivers, and deltas. The thickness range of this system is 800 feet (north-east Iowa) to 5,200 feet (southwest Iowa) (Prior et al., 2003).

The bedrock aquifer known as the Silurian-Devonian Aquifer is found all over Iowa and it mainly consists of porous Silurian dolomites and Devonian limestones and shales. Though this aquifer system has some local variation in terms of rock types, water quality and hydraulic properties it is considered as single unit (Prior et al., 2003). The unit has three carbonate layers referred to as ‘upper’, ‘middle’ and ‘lower’ aquifers. Except the upper layer all other layers are generally free from contamination (Hoyer and Hallberg, 1991). In some places this aquifer system receives water from Cedar River (Prior et al., 2003).

The deepest aquifer system in this area is the Cambrian-Ordovician aquifer situated below the Silurian-Devonian system. It is the widely used aquifer system in Iowa (Iowa DNR, 2003). This aquifer has many leaky confining beds. These leaky confining units like the Maquoketa have fractures and holes that allow infiltration from the aquifer above and below it. Jordan aquifer, the most important water-yielding layer, is part of this aquifer system. The Jordan aquifer is hydrologically connected with many other groups (Olcott, 1992).

In this area shallow wells are less than 50 feet deep and they mostly receive water from shallow alluvial aquifers. Wells ranging from 100 to 700 feet are generally located in Silurian-Devonian aquifers (Iqbal, 1996).

Soils

Among the four hydrologic soil group (A, B, C, D) in Dry Run Creek watershed group B is the most common (Shrestha, 2008; USDA, 2007). It has moderate infiltration rate, moderately fine to moderate coarse textures, and moderately well to well drained materials (USDA, 2007). The next common soil type is B/D which falls in between groups B and D. Soil group D is clay loam, silty clay loam, sandy clay, silty clay or clay with the highest runoff potential but low infiltration rate. There are very few locations in DRC watershed with soil type C. This group has properties that prevent downward movement of water. Soil group A with low runoff potential and high infiltration rates is least common in the DRC watershed area (Shrestha, 2008; USDA, 2007).

Land Use and Cover

Current land use patterns show that this creek runs through both urban and agricultural areas (Figure 12 and 13). More than 50% of the land is agricultural area. These lands are primarily used for row crop production like corn and soybeans. More than 90% of agricultural lands are used to produce corn and soybeans (Figure 12 and 13). The watershed also has residential and commercial/industrial areas (15%), forest (4%) and ungrazed grass lands (10%). The southern and western parts of the watershed are mostly agricultural areas and the northern part is mostly residential and commercial areas.

Climate and Precipitation

Temperature difference between summer and winter is very large in the study area. But in 2012 winter was surprisingly warmer compared to previous years. The lowest winter temperature was in February (31^0 F) and the highest summer temperature was 104^0 F in July. Average air temperature during the study period (May to October, 2012) was 80.25^0 F (NOAA, 2013). Precipitation data was obtained from the STORM Project (2013). Usually precipitation distribution in the area is very favorable for agriculture. Most of the precipitation occurs during the growing season (April to

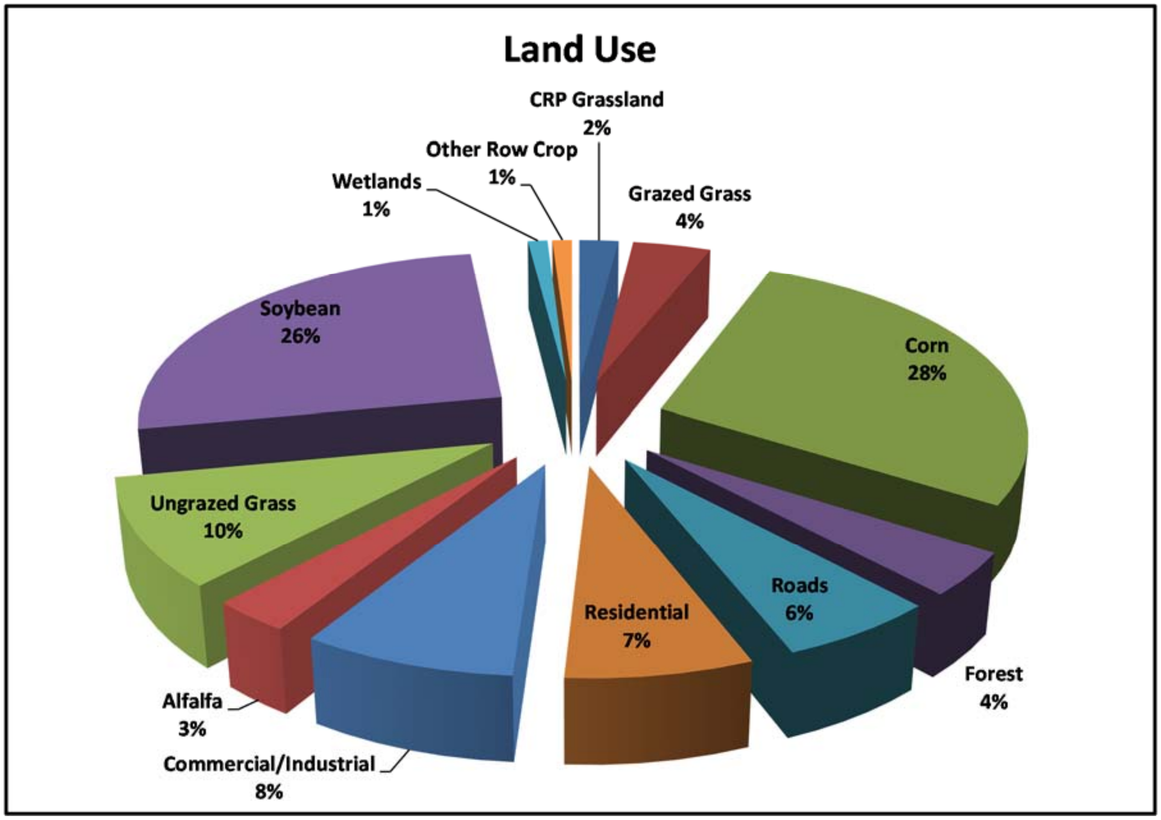


Figure 12. Land use percent in Dry Run Creek watershed (Data source: Iowa DNR, 2002).

September). Average annual precipitation in the study area is 33.15 inch but the year 2012 was very dry with total annual precipitation of 22.35 inches. It was one of the driest years in U.S. history. Figure 14 and 15 shows the precipitation data of each month during the study period (May to October, 2012). The highest precipitation occurred in May, and the lowest precipitation was observed in July (Figure 14 and 15).

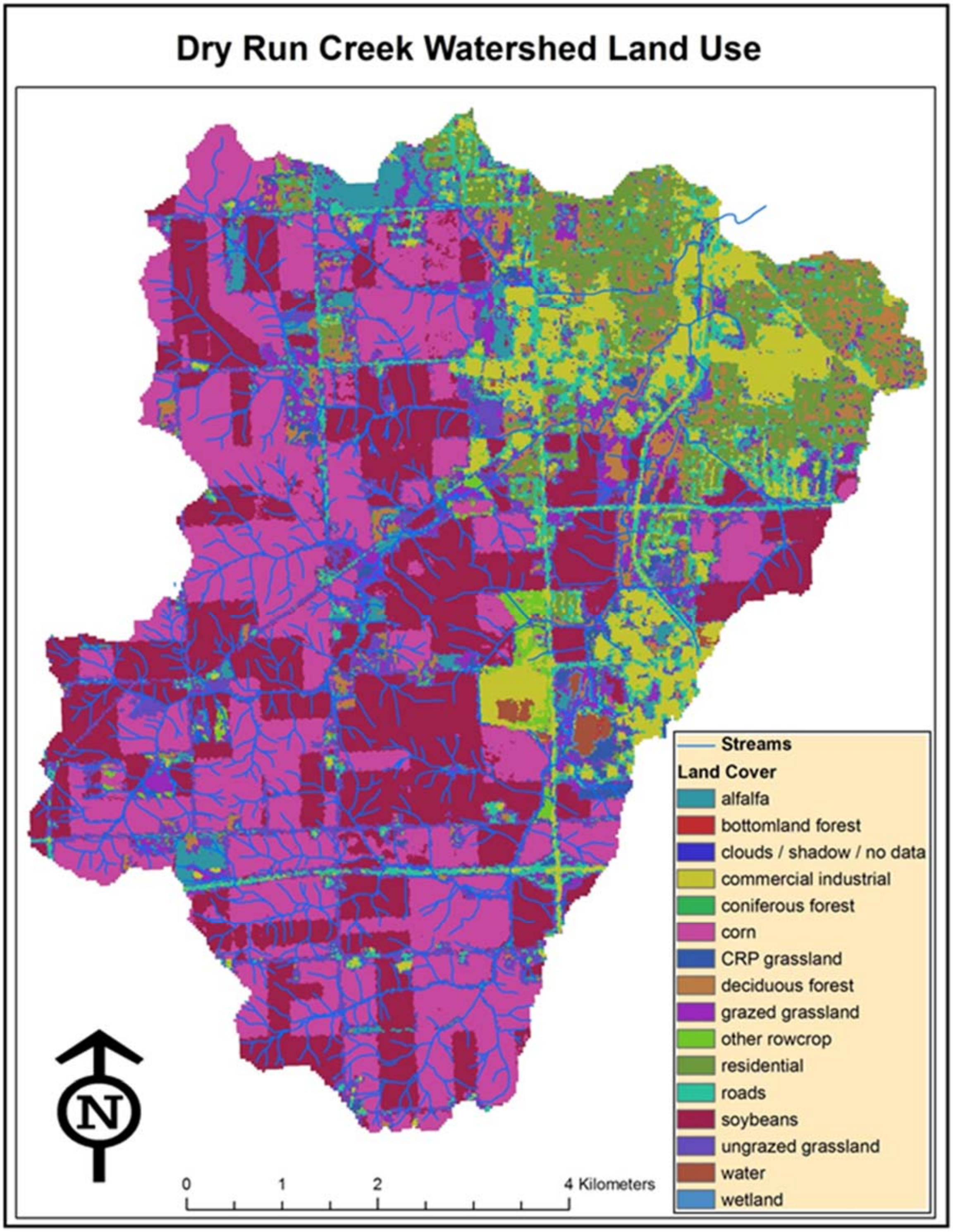


Figure 13. Land use in Dry Run Creek watershed (Data source: Iowa DNR, 2002).

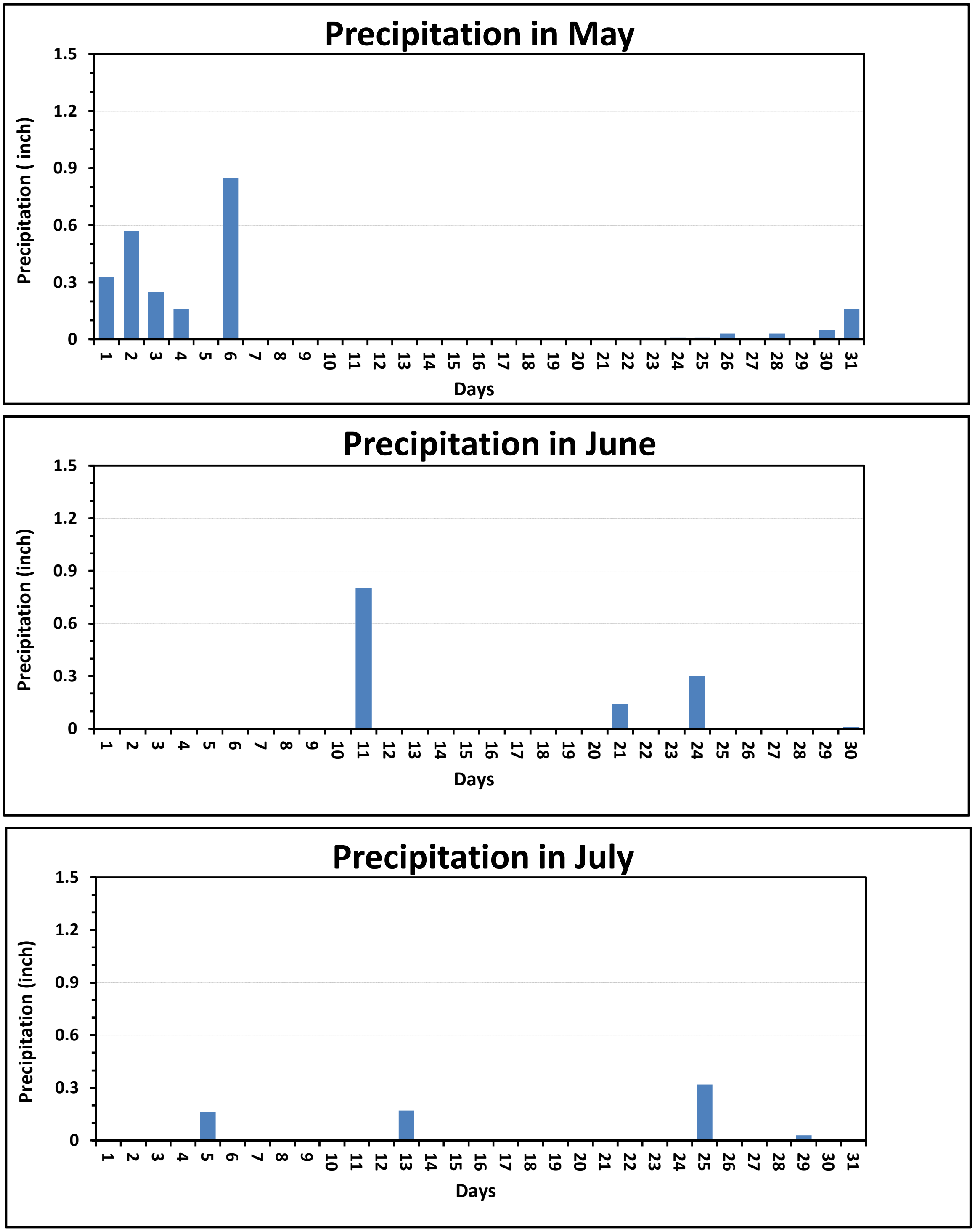


Figure 14. Precipitation during May to July, 2012.

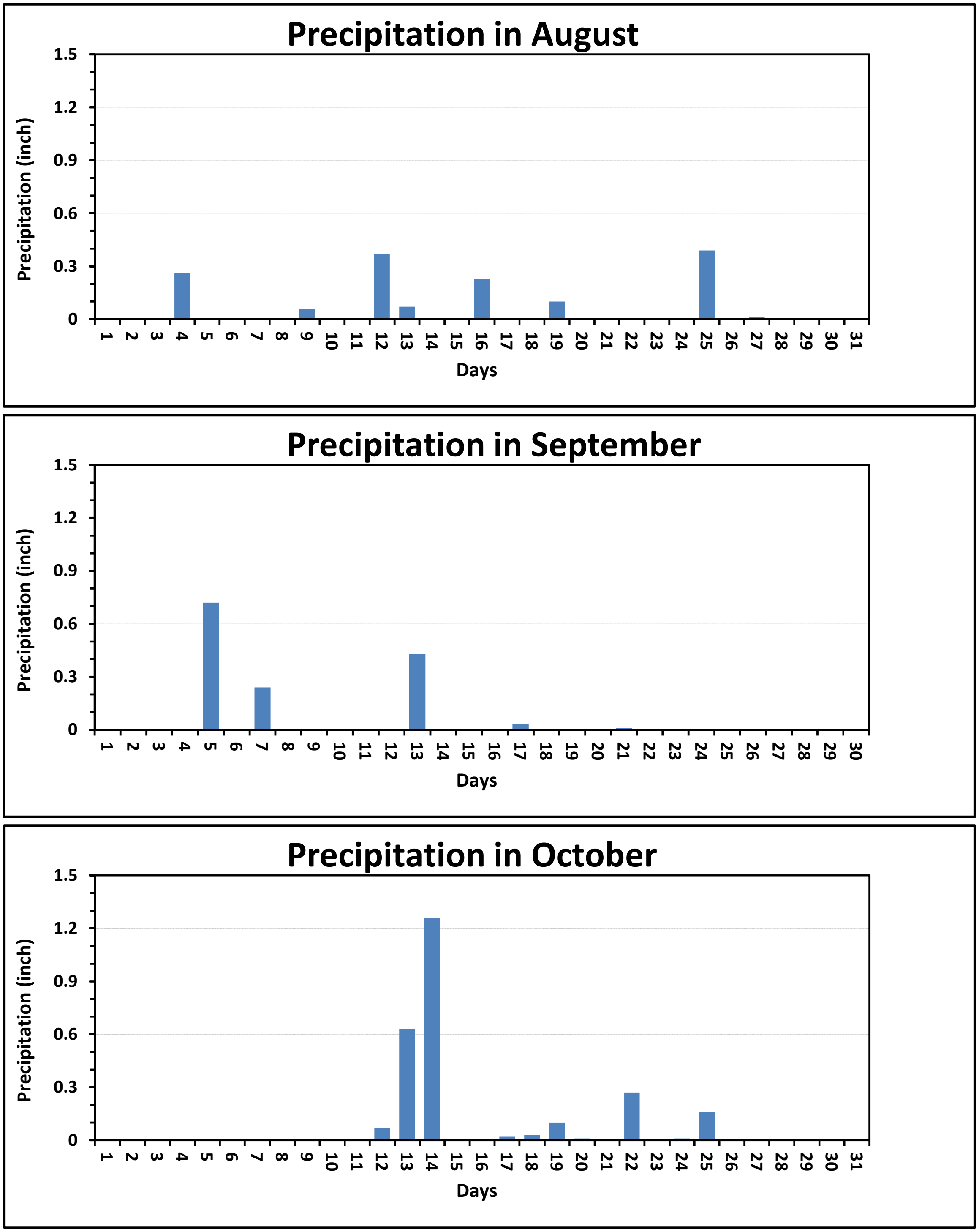


Figure 15. Precipitation during August to October, 2012.

CHAPTER 3

MATERIALS AND METHODS

Sampling Sites

A total of 43 different sites were selected throughout the DRC watershed, Cedar River, and Cedar Hills Sand Prairie for the collection of soil and/or water samples (Figure 16). Soil and/or water samples were collected from the month of May 2012 to October 2012 to represent the entire crop growing season (May to August). Sampling frequency was relatively high in the first three months (once a month). But after July, samples were collected with a two month gap in October. Samples in May 2012 were collected during the first week of the month after the snow melt and before the start of any agricultural activities for that season. The last set of samples was collected in October 2012 after all agricultural activities were done and before the snow in the following winter.

Nine sites from the agricultural areas, thirteen sites from the urban areas, twelve sites from the stream channels (including two from the Cedar River), six sites from the wetland, and three sites from the Cedar Hills Sand Prairie were chosen for sampling. Sampling sites were chosen to represent all hydrologic units within the DRC watershed and the Cedar Hills Sand Prairie. Soil samples were taken from thirty-four locations. In addition, thirty-one water samples were collected, including twenty-one surface water and ten groundwater samples. GPS locations and type of samples collected from each of the sampling sites are given in APPENDIX A.

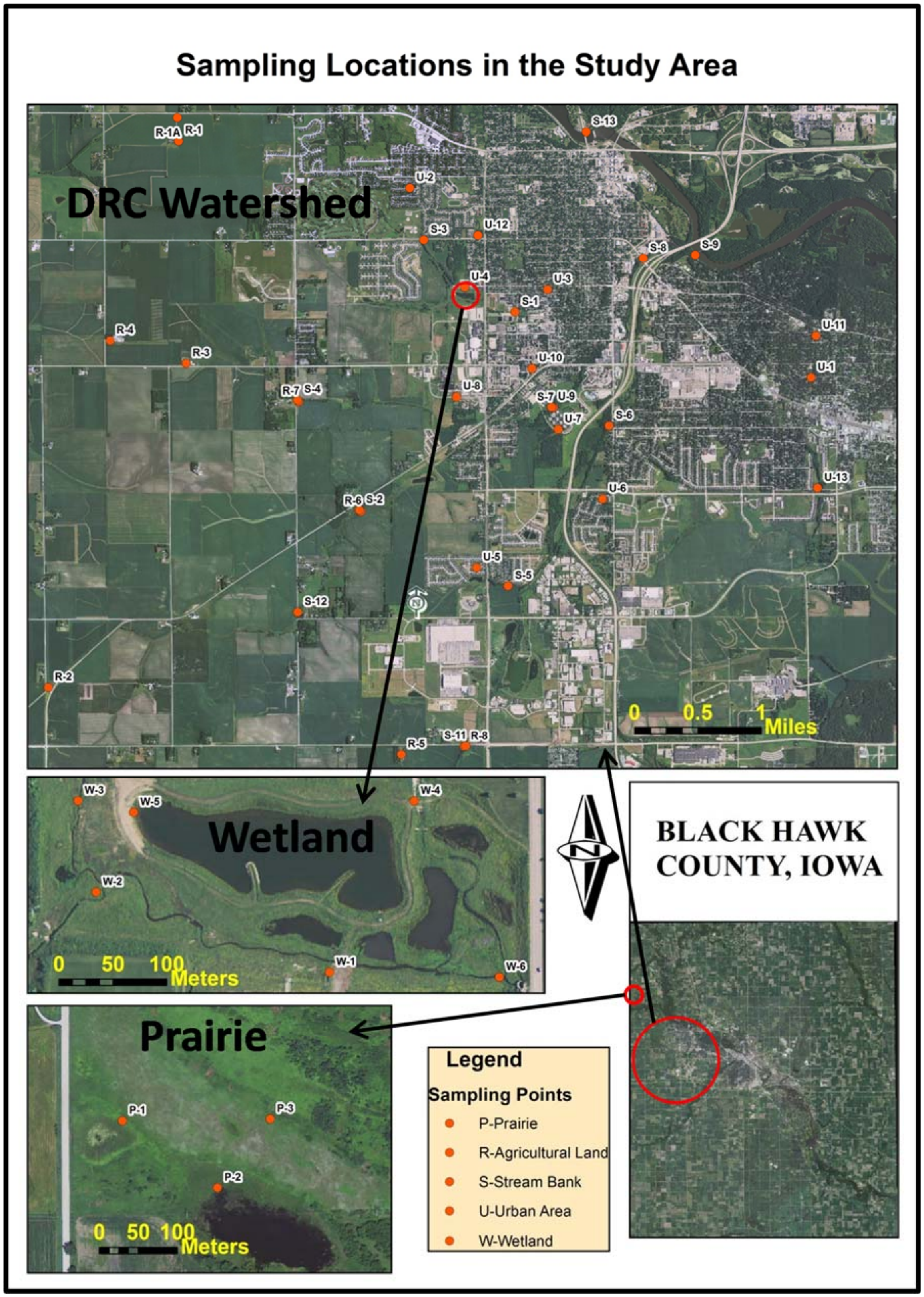


Figure 16. Sampling sites in DRC watershed and Cedar Hills Sand Prairie.

Agricultural Area

There were nine sampling sites in agricultural/rural areas within the DRC watershed, namely R-1A, R-1 to R-8 (Figure 16). Nine groundwater samples were collected from five sites (R-1 to R-5) and soil samples were collected from every site. Groundwater samples were collected from wells that were close to agricultural lands (within 100 m) and the soil samples were collected from active agricultural lands. Both groundwater and soil samples were collected once a month for the first three months (May to July 2012) and again in October 2012. Depth range of the water wells sampled in agricultural areas is 70 to 205 feet. Out of nine sites sampled, three sites were soybean fields (R-4, R-7, and R-8) and the rest of them were corn fields.

Urban Area

There were thirteen sites selected from the urban areas within DRC watershed, namely U-1 to U-13 (Figure 16). Groundwater samples were collected from five sites (U-9 to U-13) and soil samples were collected from eight sites (U-1 to U-8). Soil and groundwater samples were collected once a month from May 2012 to July 2012 and again in October 2012. Soil samples were taken from the backyard of houses at different residential areas. Groundwater samples were collected from water wells located throughout the urban areas of the watershed.

Stream Channels

There were ten sites along stream channels within the DRC watershed (S-1 to S-8, S-11, and S-12). Two additional sites were selected from the Cedar River (S-9 and S-13) (Figure 16). One of the sites (S-13) in the Cedar River was chosen from above the point where DRC enters the Cedar River main channel of DRC and the Cedar River. Another site (S-9) was chosen further downstream, below the confluence of DRC and Cedar River (Figure 16). Stream water samples were collected from the above sites once a month from May 2012 to October 2012. In addition, soil samples were collected from the stream bank once a month at nine sites (S-1, S-3, S-5 to S-9, S-12, and S-13).

Wetland

The wetland in this study is a constructed wetland, which also functions as a flood water retention area. There were six sites (W-1 to W-6) selected from the wetland (Figure 14). The wetland has four inlets, one outlet (W-6) and a central water body (W-5). Water samples were collected from all these sources once every two weeks. The southern inlet (W-1) of the wetland receives water mainly from the adjacent university facilities. Two inlets (W-2 and W-3) on the western part of the wetland are branches of DRC watershed and receive water from upstream agricultural areas. Another inlet on the northern part (W-4) is linked to other flood water retention ponds and receives water mainly from urban runoff. The wetland has one outlet (W-6) on the southeastern part where it enters into the university campus (Figure 16). Soil samples were collected from five different sites (W-1, and W-3 to W-6) once a month from May 2012 to July 2012 and again in October 2012.

Prairie

There were three sites (P-1 to P-3) in the Cedar Hills Sand Prairie (Figure 16). Soil and surface water samples were collected from all three sites once a month during May, July and October, 2012. The first two sites (P-1 and P-2) were selected from two surface water bodies within the prairie and the third site (P-3) was selected from a small fen in the center of the prairie (Figure 16).

Methods

Onsite Parameters and Water Sampling

Every time at each well site, water was collected from the aquifer. For this, standard sampling procedure was followed. At the beginning the water pump was run for a few minutes to let the water flow to make sure that the water was coming from the aquifer. Usually at the beginning water temperature was low and after few minutes it increased, indicating that the water was coming from the aquifer instead of the pipes. All probes were rinsed with the well water before taking any measurements. First, the temperature was measured, followed by dissolved oxygen (DO), total dissolved solids (TDS), conductivity, turbidity, and pH. DO was measured with a HACH HQ30d Meter and LDO probe. Temperature, TDS and conductivity were measured using HANNA HI98311 probe. Turbidity was measured using a 2020i LaMotte Turbidity Meter and pH was measured with a Extech S/N 33214 ExStik II. The same procedures were followed for the surface water measurements (Figure 17). Surface water samples were taken from the main stream channel and larger water bodies.

Water samples for lab analysis were collected in 125 ml high density polyethylene (HDPE) plastic bottles. Each bottle was rinsed three times with the water to be sampled before filling the bottle. All bottles were labeled with site number and date and stored in a refrigerator about two months for lab analysis. Water samples to measure total suspended solids (TSS) were collected in 1 L HDPE bottles.

Figure 17. In situ surface water parameters measured in the field.

Soil Sampling

A 12 inch soil profile was collected from each site every time with the help of a stainless steel soil probe (Figure 18). The soil probe was pushed into the ground vertically by manual pressure. Soil samples were collected at 0 inch (surface), 6 inch, and 12 inch depths separately and placed into a Ziploc plastic bag with proper labeling. All soil samples were stored in a refrigerator about two months for lab analysis. Soil moisture content was also measured in field condition with a digital soil moisture meter (DSMM500) (Figure 18).

In-situ Infiltration Test

In situ water infiltration tests were conducted to determine the infiltration rates at different parts of the DRC watershed and the Cedar Hills Sand Prairie. The top 8 inches of soil was removed by using a 2.5 inch inside diameter stainless steel pipe to avoid the influence of surface fracture and vegetation roots system. The stainless steel pipe was pushed vertically with manual pressure. This made an 8 inch deep and 2.5 inch diameter

Figure 18. Soil sample collection. a) soil probe, b) digital soil moisture meter, c) a soil profile, and d) soil samples in ziploc bags.

hole in the ground. Then water was poured into the hole to record its infiltration rate into the subsurface. A stop watch and a ruler were used to measure the volume of water (hole diameter was known so the drop in water level was used to calculate the water volume) infiltrating in a given time (Figure 19). The same method was used every time for other locations. Infiltration rates were finally presented by calculating the drop of water level per unit time.

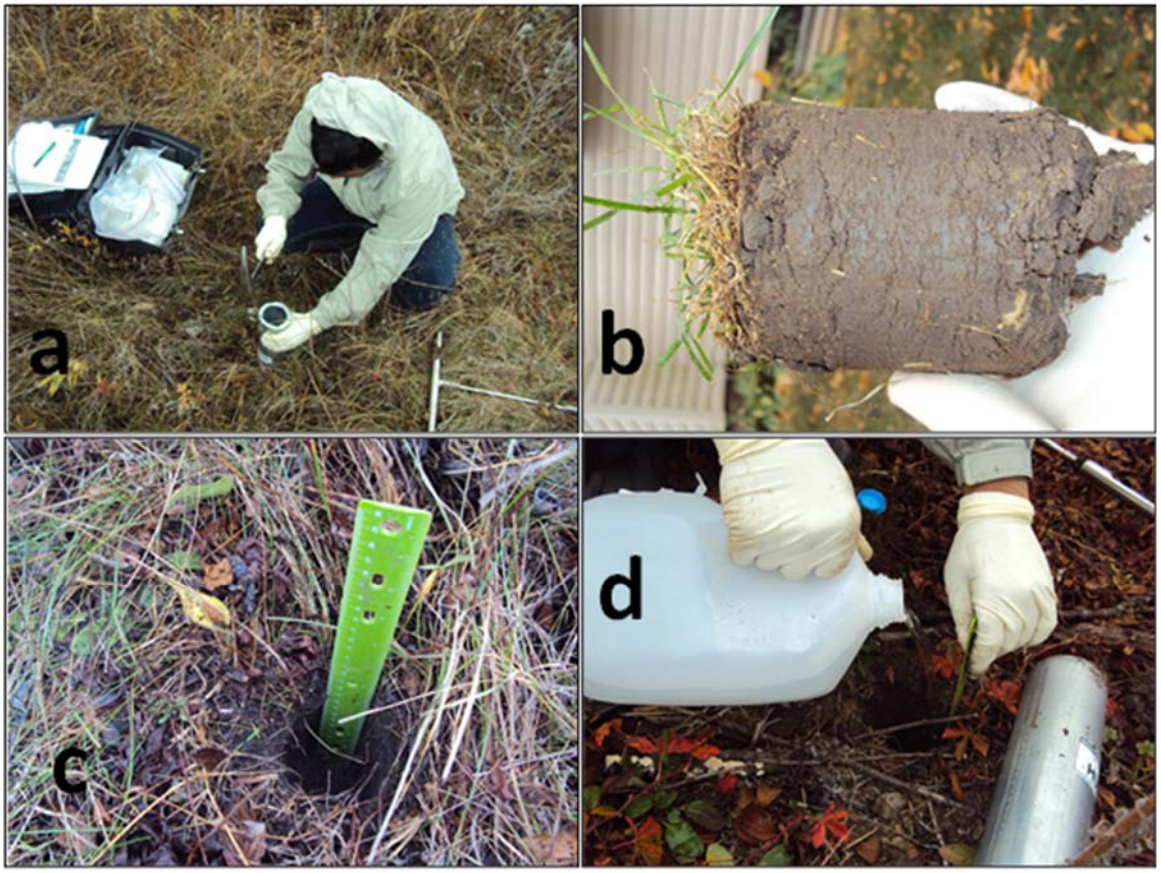


Figure 19. In situ infiltration test. a) Inserting the pipe, b) soil cover removed, C) measuring scale, d) pouring water.

Stream Discharge

Discharge measurements were done by Jennnifer Shepeck, a graduate student in the Environmental Programs at UNI, from May 2011 to August 2011. She did the measurements once a week over several months and the data were collected from her to calculate the nutrient loads at different points of Dry Run Creek.

Discharge was measured in 10 sampling sites (S-1 to S-8, S-11, and S-12) within the DRC watershed. During each measurement, the width of the stream was divided into three segments. In each segment, depth and velocity were measured. Depth was measured with a meter stick and velocity was measured with a flow meter at the middle of each segment. Subsequently, depth and velocity were multiplied to obtain the discharge of that segment. Discharges from all three segments were then added to calculate the total discharge of the stream.

Watershed Delineation

Shrestha (2008) divided the DRC watershed into several sub-watersheds that receive flow at a given point. Sub-watersheds were created from a Digital Elevation Model (DEM) of the watershed by computing the flow direction and using it in the watershed tool in the Hydrology Modeling toolbar (a third party extension to ArcGIS). The area of each sub-watershed was also calculated. In this study, sub-watersheds (Figure 20 and 21) delineated by Shrestha (2008) were used to predict nutrient contribution of different parts of the DRC watershed as well as to calculate total loads.

Load Calculation

Total nutrient loads were measured by calculating how much nutrient was passing with water through a particular stream section. For this calculation, stream discharge was multiplied by the dissolved nitrate concentration in water. Subsequently, loads of P and N were calculated. TSS loads were calculated by multiplying stream discharge and TSS concentration in the stream water. Due to the limitation of time and resources, measurement of stream discharge and dissolved chemical constituents had not been done more frequently than every two weeks. Thus the calculations are expected to provide only a general idea about the fate and transport of nutrients.

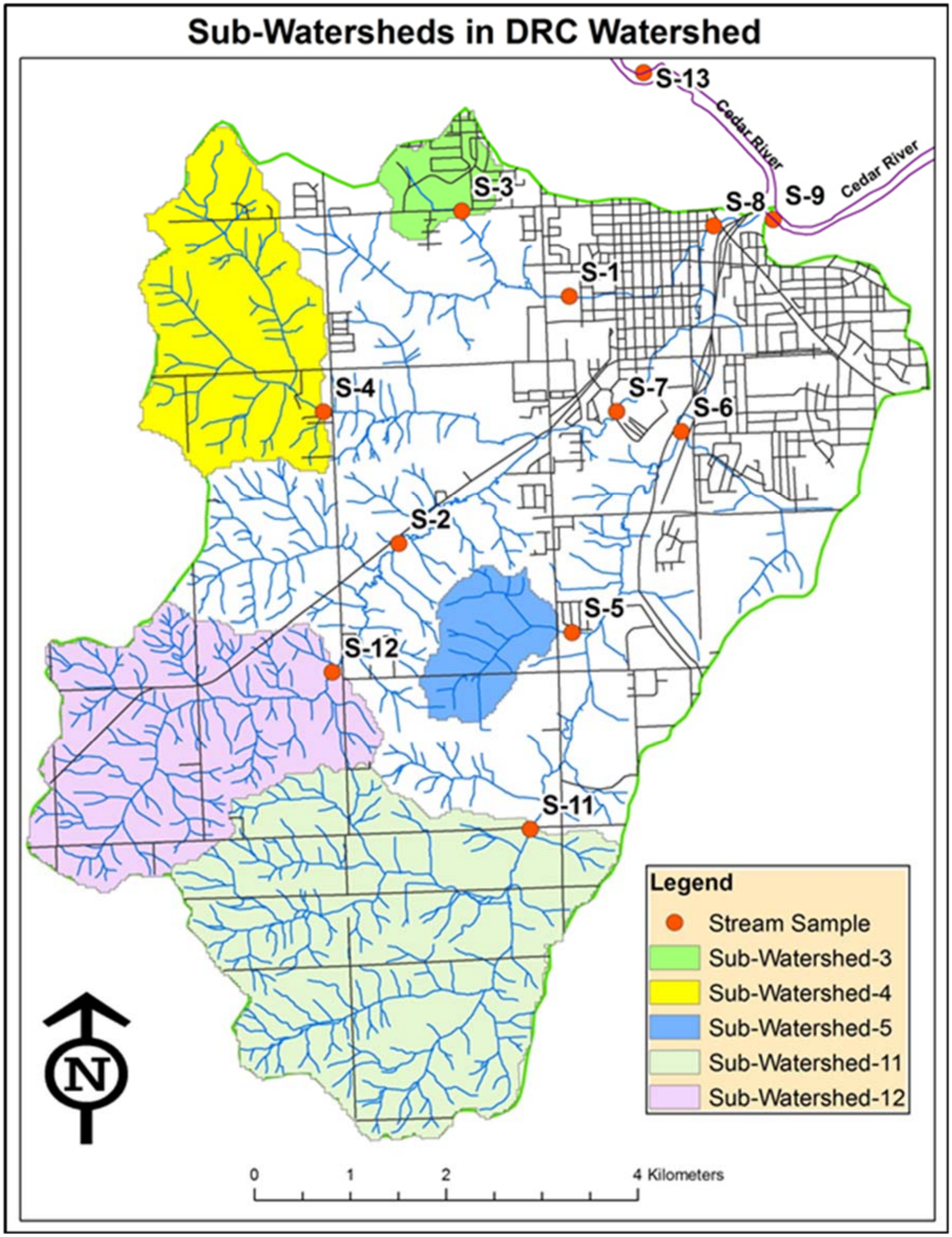


Figure 20. Sub-watersheds in DRC watershed for locations S-3, S-4, S-5, S-11, and S-12 (modified from Shrestha, 2008).

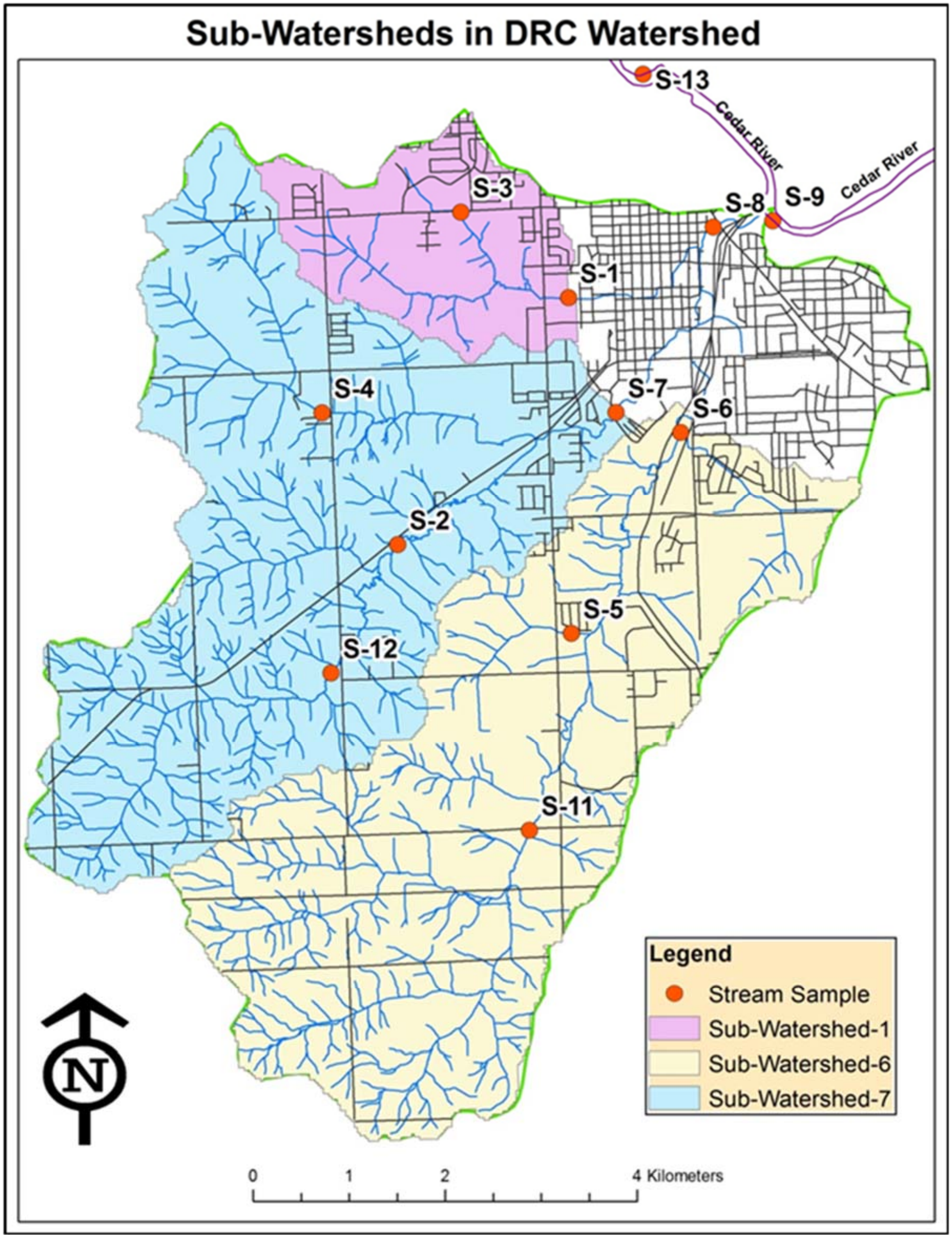


Figure 21. Sub-watersheds in DRC watershed for sampling points S-1, S-6, and S-7 (modified from Shrestha, 2008).

Lab Analysis

Anions

Chloride, nitrate and sulfate were analyzed using an ion chromatograph (Dionex, Model DX-120). The Dionex DX-120 ion chromatograph performs isocratic ion analysis applications using conductivity detection. The chromatograph is a high precision ion analyzer where retention peaks are directly observed on the monitor as the sample runs.

The samples were taken out of the refrigerator and stored at room temperature for 8-10 hours before analysis. The flow rate was set at 1.75 ml/min. Known standards of target anions (5, 25, 50 ppm) were used for machine calibration, and a 25 ppm standard solution was used to check the validity of the calibration. Samples were poured into 5 ml poly vials manually and sealed with 20 μm filter caps to prevent any cross contamination. Poly vials were then placed into Dionex AS40 automated sampler to run the samples automatically by the ion chromatograph. Total analysis time for each sample was about 8 minutes. The analytical margin of error was ±0.5 mg/l.

Soil Nitrate Extraction

Nitrate is highly soluble in water. Soil nitrate extraction is relatively simple and there are various different methods that exist for its extraction. Griffin et al. (1995) mentioned that water or dilute salt solutions can be used to extract nitrate from most soils because essentially all the nitrate in soils with low anion exchange capacities is water soluble. Gelderman and Beegle (1998) mentioned that extraction of soil nitrate with water is possible for most soils of the North Central region of the US. Many researchers from different countries and regions also used water as a successful extractor of soil nitrate (Kim et al., 2006; Schmidhalter, 2005; Stalikas et al., 2003).

For the extraction of soil samples deionized water was used. Five grams of wet soil were taken in a 250 ml Erlenmeyer flask with 150 ml deionized water to extract both pore water nitrate and soil nitrate. Then the soil-water mixture was left at room temperature for 24 hours to make sure the soil was fully disintegrated and there were no compacted soil aggregates. After 24 hours the mixtures were put into an automatic shaker (Figure 22) at 200 RPM (revolutions per minute). Previous studies showed that maximum one hour shaking is good enough (Kim et al., 2006; Schmidhalter, 2005; Stalikas et al., 2003) but to make sure all soil nitrate had been extracted samples were left on the shaker for 6 hours. After shaking, the mixtures were filtered through 0.45 μm membrane filters by using a vacuum pump to separate the soil (Figure 22). The filtered water samples were kept in HDPE bottles and refrigerated for about two months for ion analysis.

A set of soil samples was used to compare the results of extraction among water and other standard methods. For this, 2M KCl was used as standard extractor as described by Griffin et al. (2009). Extraction with 2M KCl was done by first soaking the samples in KCl for 6 hours and then shaking it for 30 minutes at 200 RPM. After shaking, soil was filtered out by the same method described above. Each sample was extracted using both methods to compare the results.

Total Phosphorus

For total phosphorus (TP) analysis in the laboratory, the analysis was done in two steps (Clesceri et al., 1998). In the first step, called persulfate digestion method, all

Figure 22. Soil nitrate extraction. a) soil water mixture. b) automatic shaker. c) vacuum pump used for filtration. d) filtration of soil water mixture after shaking.

phosphorus in the sample was converted to orthophosphate. In this step, for water, 50 ml of each sample was taken into a 125 ml Erlenmeyer flask. For soil, samples were first oven dried for 24 hours at 110°C and 1.5 g of dried soil from each sample was taken into the 125 ml Erlenmeyer flask with 50 ml of deionized water. Then 1 ml of sulfuric acid solution (300 ml H_2SO_4 in 1 L) and 0.5 g of potassium persulfate were added to each sample (both soil and water). Aluminum foil was used to cover the flasks before the samples were autoclaved for 30 minutes.

A solution of 250 µg PO_4^{3}-Pwas used as standard solution. This solution was prepared by diluting 1097.5 mg of anhydrous potassium phosphate monobasic (KH_2PO_4) to 1 L deionized water. Standards of 0, 125, 250, 500, 750, 1000 µg P for soil and standards of 0, 1, 2, 5, 10, 25, 50 µg P for water were then made and treated the same way as the samples.

The second step was ascorbic acid assay method. In this step orthophosphate was converted to a molybdenum blue complex to give a blue color that can be measured using a spectrophotometer. After autoclaving, all water samples were taken into a 100 ml volumetric flask. For soil, the samples were first centrifuged to separate the soil from water. The water was then taken into 100 ml volumetric flasks. Subsequently, 1-2 drops of phenolphthalein indicator was added to each flask. The samples and the standards were titrated with 1N NaOH (10-15 ml) solution to neutralize and they turned into pink color after neutralization. The samples and standards were then diluted by adding deionized water to the 100 ml mark. Each sample was shaken to mix the solution.

The mixed-reagent was prepared by mixing 250 ml of 4N H_2SO_4, 25 ml of potassium antimonyl tartate solution (dissolved 2.2 g $K(SbO)C_4H_4O_62H_2O$ in 500 ml deionized water), 75 ml of ammonium molybdate solution (20 g $(NH_4)_6Mo_7O_{24}4H_2O$ in 500 ml deionized water) and 2.16 g ascorbic acid in a 500 ml volumetric flask. Extra space of the flask was filled up to the level with deionized water. For soil samples, 10 ml mixed-reagent was added to 15 ml of sample and 25 ml deionized water in a 50ml volumetric flask. For water samples, 10 ml mixed-reagent was added to 40 ml of sample in a 50 ml volumetric flask. The last reaction took about 10 to 30 minutes to complete and turn the sample into a blue color. Finally, intensity of the blue color was measured using a spectrophotometer (GENESYS ^{TM}) set at the wavelength of 880 nm.

Soil Organic Matter

All soil samples were analyzed to determine the organic matter content by the loss-on-ignition method (Schulte and Hopkins, 1996). Approximately 10 g of soil was taken from each sample in weighted and numbered crucibles. Samples were oven dried at 110 °C for 24 hours. Crucibles with dried samples were measured to get the dry weight of the sample. Then crucibles with samples were placed into a muffle furnace for combustion. This was done in three steps; in the first step the temperature was set to 200 °C for 2 hours. In the second step, the temperature was set to 375 °C for another 2 hours. Finally, in the third step, the temperature was set to 550 °C for 1 hour. These steps were done one after another without any break. Crucibles were then removed from the furnace and cooled at room temperature for a few hours and the weight of the crucibles with the samples was measured. The dry weight of soil was calculated by subtracting the total weight of the crucible and the sample. Soil weight after combustion was calculated by subtracting the crucible weight from the total weight of crucible and sample after combustion. The soil organic matter percentage from the loss-on-ignition method was estimated by the following equation (Schulte and Hopkins, 1996):

Soil organic matter percentage = [(soil weight after combustion – oven dry soil weight)/oven dry soil weight] x 100

Total Suspended Sediments

Total suspended sediment (TSS) concentrations were determined by filtration (Clesceri et al., 1998). From each sampling site, 1 liter water sample was filtered through a pre weighted glass fiber filter by using a vacuum pump. The filters allow the water to pass through and collect the suspended sediments on top of it. After filtration, the glass filters with residue were collected and oven dried at 103-105 °C for 1 hour. The filters were then kept at room temperature for few minutes to cool down and reweighed. The difference between the pre-weighed filter and the reweighed filter gave the weight of suspended sediments. Finally, TSS concentration was calculated by using the formula: TSS (mg/l) = [{Wt. of (Filter + Sediments) – Wt. of Filter}/ Volume of sample (ml)] x 1000

Data Analysis

Data were analyzed for both temporal and spatial variations. Mean, average, maximum, and minimum were calculated for different parameters. Data were plotted into maps using GIS. Temporal graphs were drawn by using MS Excel to see the changes during the sampling period.

CHAPTER 4

RESULTS AND DISCUSSION

Onsite Parameters

Temperature

Temperature has an important influence on water chemistry. Water temperature can increase or decrease chemical reactions and impact biological activities. Also, solubility of minerals depends on temperature. In general, solubility of minerals increases with increase of water temperature (USGS, 2013 b). Some gases, such as oxygen and carbon dioxide show high solubility with decreasing temperature. For example, dissolved oxygen (DO) increases as water temperature decreases (USGS, 2013 b).

In this study, temperature fluctuation patterns and ranges were different in different hydrologic units (Figure 23). In stream locations, all sites showed comparable fluctuation patterns with a range of 11 °C to 25°C. All sites showed relatively high temperatures during July with the highest temperature of 25.3 °C at S-13. Both June and October showed low temperatures in all sites. The lowest temperature (11°C) was observed at site S-13 during October.

In wetland locations, temperature ranged from 9° C to 29°C (Figure 23). The highest temperature of 29°C was observed at site W-5 in July and the lowest (9°C) was observed at site W-6 in October. Temperature was mostly above 20° C until July and then it dropped below 13° C in October. Temperature change throughout the wetland was uniform and consistent. Factors like flow of water, vegetation and source of water might have influenced the variations in water temperature.

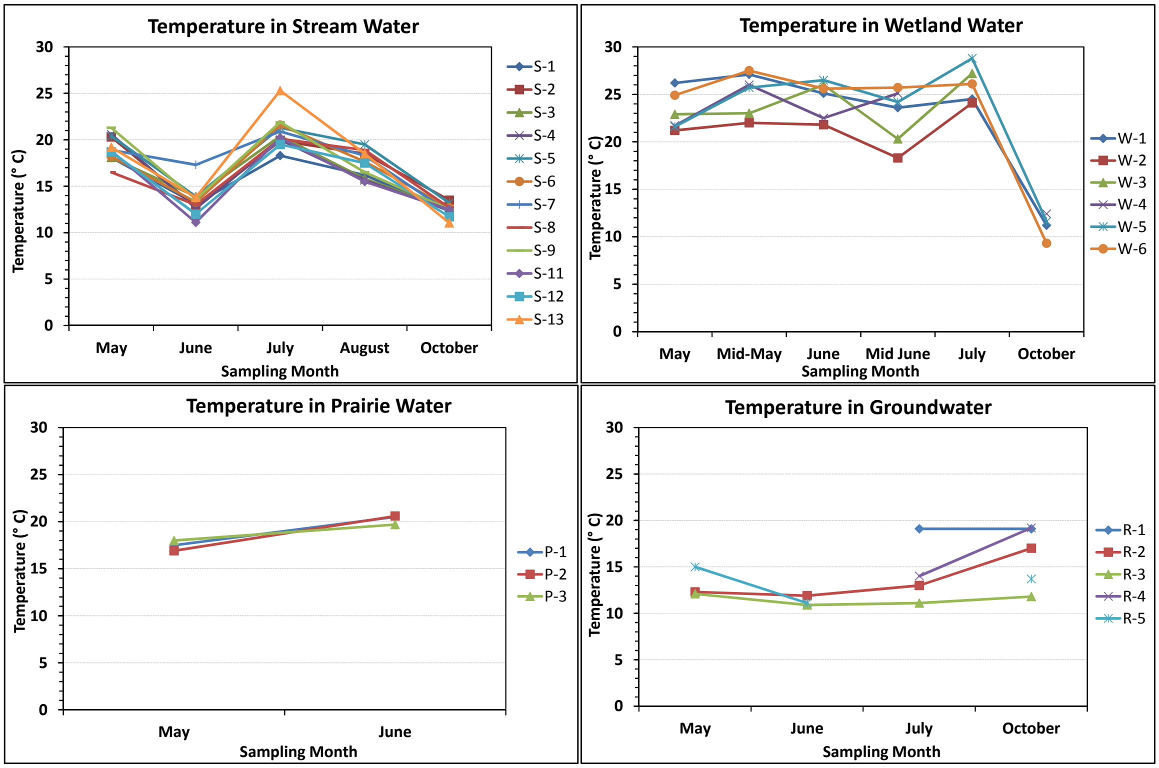


Figure 23. Temperature in different hydrologic units.

Groundwater temperature didn't fluctuate as much as the surface water. The range of groundwater temperature was between 9° C and 19° C. The highest temperature was observed at site R-1 in July and the lowest at site R-3 in June. Groundwater temperature was generally low compared to surface water until it started to rise slightly in late July at most sites (Figure 23).

These ranges of surface water temperature are very much similar to what has been reported by IOWATER (IOWATER, 2010). In surface water, wetland locations were warmer as compared to other hydrologic units. Stream water was cooler as compared to wetland and prairie. This may be due to the vegetation cover along the stream channel and flow of water that promotes the distribution of heat energy. Groundwater temperature was relatively low compared to surface water. Also, groundwater temperature was mostly uniform because it is in a close system.

Dissolved Oxygen

Dissolved oxygen (DO) is the amount of oxygen dissolved in water. It is a very important parameter of a water body to support aquatic life. Concentration of DO is perhaps the single most important feature of water quality. It is an important regulator of chemical processes and biological activities in water. Cold water can hold more DO than warm water (USGS, 2013 c).

In stream water, DO ranged in May and June from 7.8 to 10.5 mg/l. Overall, the DO concentration decreased in July, except in site S-13, with a range of 4.8 to 11.8 mg/l. DO values subsequently increased in August and October with a range of 6.5 to 9.6 mg/l and 8.1 to 11 mg/l respectively (Figure 24). The highest DO value was observed at site S-13 in July and the lowest value was observed at site S-2 also in July. The DO values in stream sites nicely followed the inverse relation with water temperature except in one reading at site S-13 in July (Figure 24). It is unclear why DO increased in that site with the increase of temperature.

In wetland locations, DO ranged from 4 to 17.3 mg/l (Figure 24). The highest DO value of 17.3 mg/l was observed at site W-3 in July and the lowest value of 4 mg/l was also observed at site W-3 in mid-June (Figure 24). The DO values changed inversely with the change of water temperature (Figure 23 and 24). But in few sites like W-3, W-4, and W-5 where water had little or no flow, the relation was the opposite. That is, DO value

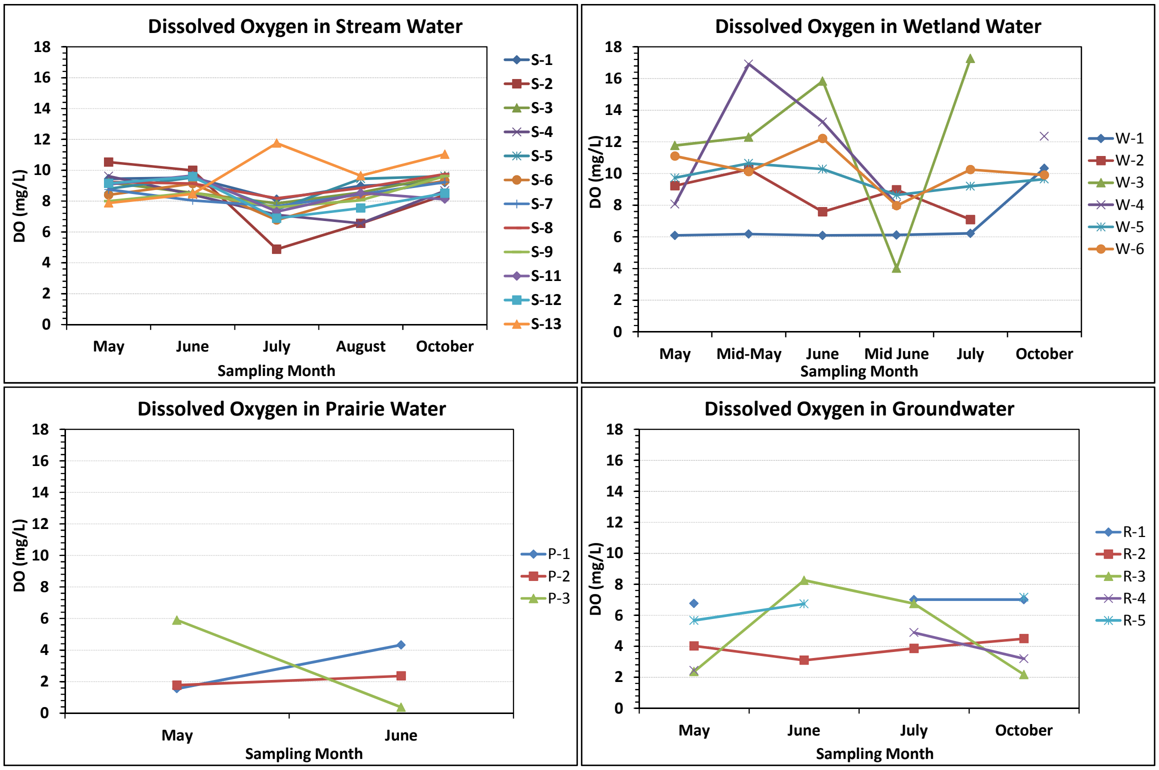


Figure 24. Dissolved oxygen (DO) in different hydrologic units.

increased with the increase of water temperature and the value decreased with the decrease of water temperature (Figure 23 and 24). The increase of DO value with water temperature during June might be an effect of oxygen released through photosynthesis. The decrease of DO with water temperature during July is attributed to the activity of organisms and decomposing processes of plant materials where oxygen is consumed to produce CO_2.

The range of DO in prairie was from 0.3 to 5.9 mg/l. Both the highest and the lowest values were observed at site P-3 in May and June respectively. No surface water was found in prairie locations after June. Except site P-3, DO value increased with the increase of water temperature. This might be an effect of the oxygen released via photosynthesis.

The range of DO in groundwater was 2.1 to 8.2 mg/l. Both the highest and the lowest values were observed at site R-3 in June and October respectively (Figure 24). At site R-3, the DO value suddenly increased to above 8 mg/l. The water well in site R-3 is 70 feet deep and it is expected to be connected with the surface water by bedrock (carbonates) fractures. The well is within 20 ft of the DRC.

The observed levels of DO in surface water (stream and wetland) were generally higher in comparison to ground water (Figure 24). Iowa has a water quality standard of 5 mg/l of dissolved oxygen for warm water streams and 7 mg/l for cold water streams to support aquatic life (IOWATER, 2010). Excluding the 4.8 mg/l at S-2 in July and the 4 mg/l at W-3 in Mid-June the DO levels are all above this limit. Low DO in prairie indicates high microbial activity and favorable condition for denitrification. High DO concentrations in bed rock aquifers are unlikely to support denitrification.

pH

The pH scale ranges from 0 to 14 and denotes various degrees of acidity or alkalinity. Since pH values are expressed in logarithmic scale, difference of H^+ concentration between two successive units is ten times higher or lower. pH plays an important role in chemical reactions and also influences aquatic biota (including composition). Photosynthetic uptake of CO_2 can increase pH value while decomposition/respiration can decrease it (USGS, 2013 d).

In stream water, pH was within a very narrow range of 7.8 to 8.7 (Figure 25). Except the highest value at site S-13 in October and next highest value of 8.6 at site S-3 in June, all other measurements were within the range of 7.8 to 8.4. The lowest pH value was observed at site S-2 in October. Fluctuations of pH values were more or less consistent in all sites. pH in the streams of Iowa tends to be slightly higher than other areas due to the underlying limestones. The pH values in Iowa streams are commonly from 8 to 8.4 (IOWATER, 2010). Slightly higher pH values in June might be the effect of lime application in agricultural fields and application of limestone gravels in rural roads.

In wetland water, pH was within a range of 7.5 to 8.8 (Figure 25). The highest value was observed at site W-5 in October and the lowest was observed at site W-4 in June. In general, pH values showed an increasing trend from May to October. In sites W-2 and W-3, pH values followed the trend of DO values (Figure 24 and 25). As mentioned earlier, DO values of these sites didn't show the usual relationship with temperature (Figure 23 and 24). This might be the influence of photosynthesis and respiration/decomposition on pH and DO values.

pH of prairie water ranged from 6.1 to 6.7 with the highest value at site P-3 in June and the lowest value at P-2 in May (Figure 25). pH values didn't change much within each site and in the area. No human activity and increased levels of microbiological activities might have reduced the DO and pH values in the prairie (Figure 24 and 25).

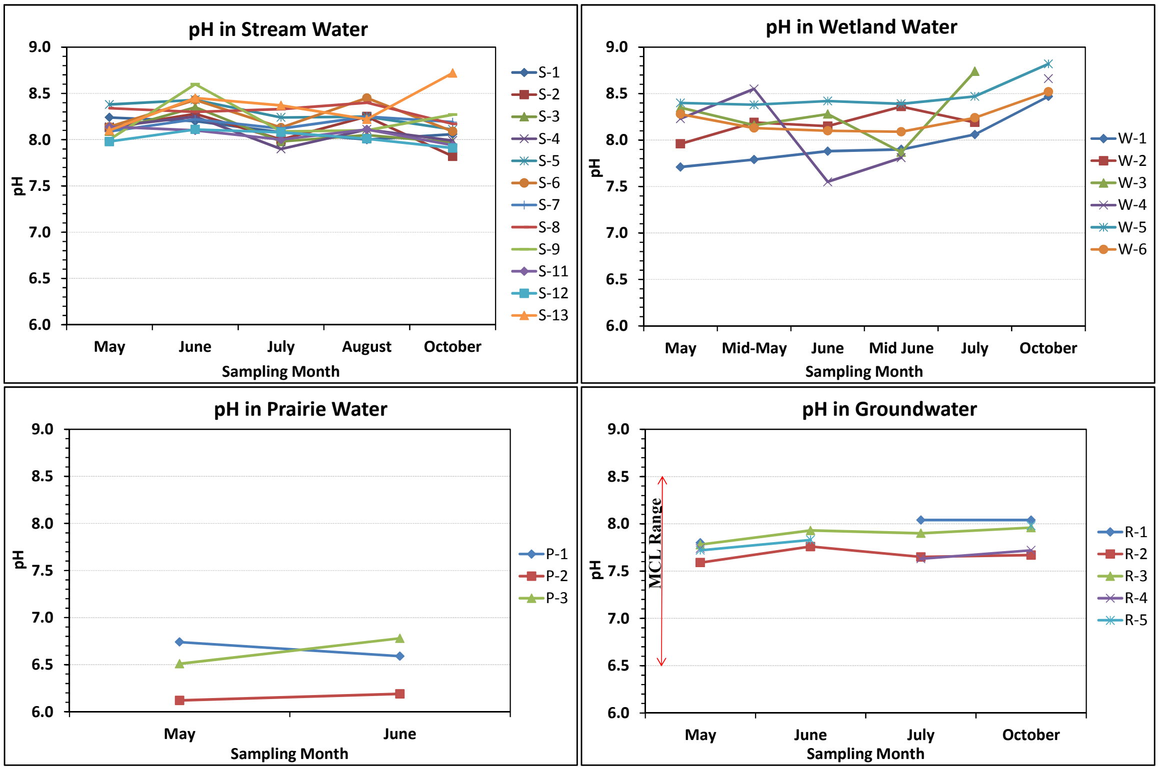


Figure 25. pH values in different hydrologic units.

Groundwater pH ranged from 7.6 to 8.1 with the highest value at site R-1 in July and the lowest value at site R-2 in May (Figure 25). In each location groundwater pH was uniform and didn't show any considerable change. This range of pH was expected in this area of carbonate bedrock. The buffering capacity of calcites as well as dolomites makes the water relatively more basic. The national secondary drinking water standard for pH is 6.5 to 8.5 (U.S. EPA, 2013 b). None of the groundwater samples violated the EPA maximum contaminant level (MCL) of pH.

Except in prairie locations, all surface water bodies had pH values around 8. Values in wetland showed many variations compared to stream values. In fact, the pH values in prairie were the lowest among all hydrologic units, expectedly due to organic decay process. Groundwater pH was mostly below 8 but above 7.5.

Total Dissolved Solids

Total dissolved solids (TDS) includes all inorganic and organic dissolved substances in water. The main sources for TDS in water include agricultural and residential runoff, leaching of soil contamination and discharges from industrial or sewage treatment plants. Major components of water TDS are calcium, phosphates, nitrates, sodium, potassium and chloride (Carpenter et al., 1998; Mullaney et al., 2009).

In stream water, TDS ranged from 332 to 456 mg/l in May, 248 to 430 mg/l in June, 286 to 529 mg/l in July, 289 to 450 mg/l in August, and 117 to 360 mg/l in October (Figure 26).

The highest TDS value was observed at site S-6 in July and the lowest TDS was observed at site S-9 in October. TDS was generally high in July. During this time there were few rain events that brought dissolved materials into streams (Figure 14). May, June and August showed similar kinds of TDS values. After August there was a sharp decline in TDS. This might be the effect of relative dryness and the lack of agricultural activities. Commonly, agricultural fertilizers and eroded soils contribute dissolved materials to surface runoff. Site S-8, where DRC meets with the Cedar River (Figure 16), showed lower TDS values compared to site S-13 farther upstream (Figure 16) except in May and July (Figure 26).

In wetland locations, TDS ranged from 316 to 441 mg/l in May, 280 to 456 mg/l in Mid-May, 258 to 391 mg/l in June, 307 to 400 mg/l in Mid-June, 224 to 437 mg/l in

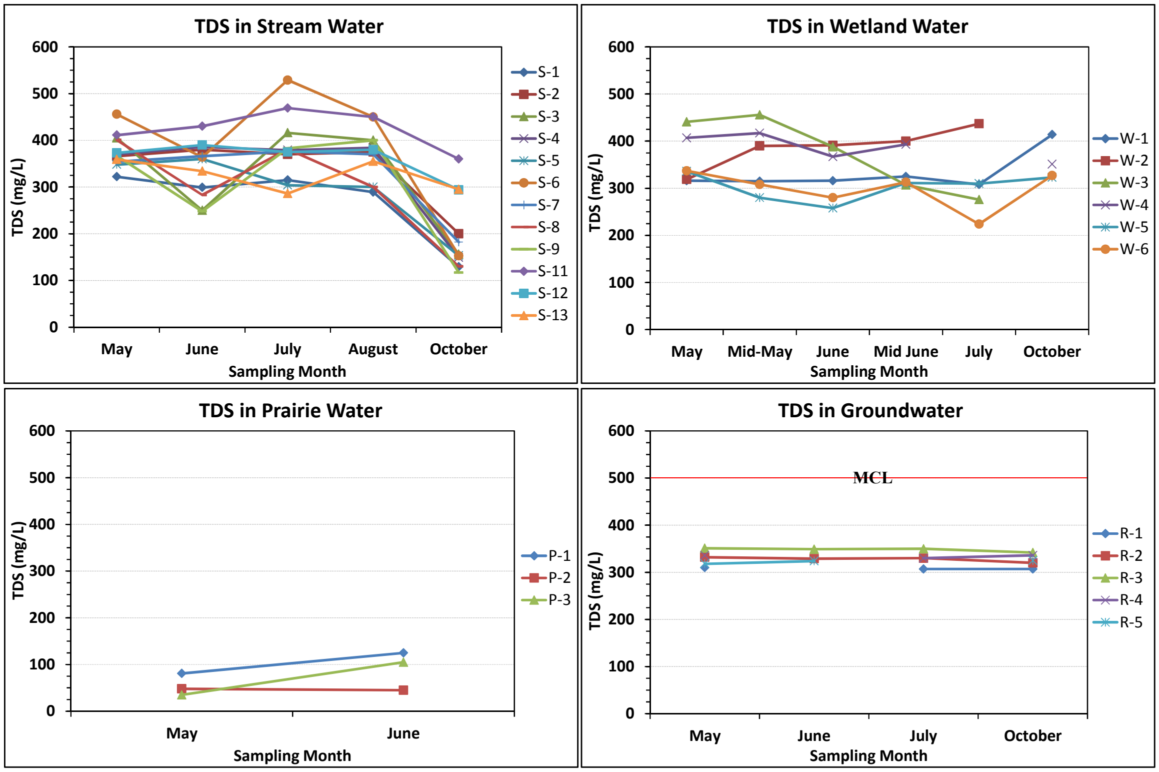


Figure 26. Total dissolved solids (TDS) in different hydrologic units.

July, and 323 to 414 mg/l in October (Figure 26). The highest TDS value was observed at site W-3 in Mid-May and the lowest value was observed at site W-6 in July (Figure 26).

In prairie, TDS values were within the range of 35 to 125 mg/l (Figure 26). The highest TDS was observed at site P-1 in June and the lowest at site P-3 in May.

Groundwater TDS was consistent during the study period with a range of 307 to 351 mg/l (Figure 26). According to EPA, MCL for drinking water TDS is 500 mg/l (U.S. EPA, 2013 b). None of the groundwater samples exceeded the MCL.

Figure 27 shows the temporal and spatial distributions of TDS within different sub-watersheds (Figure 20 and 21). In sub-watershed-6, site S-11 and S-6 were the

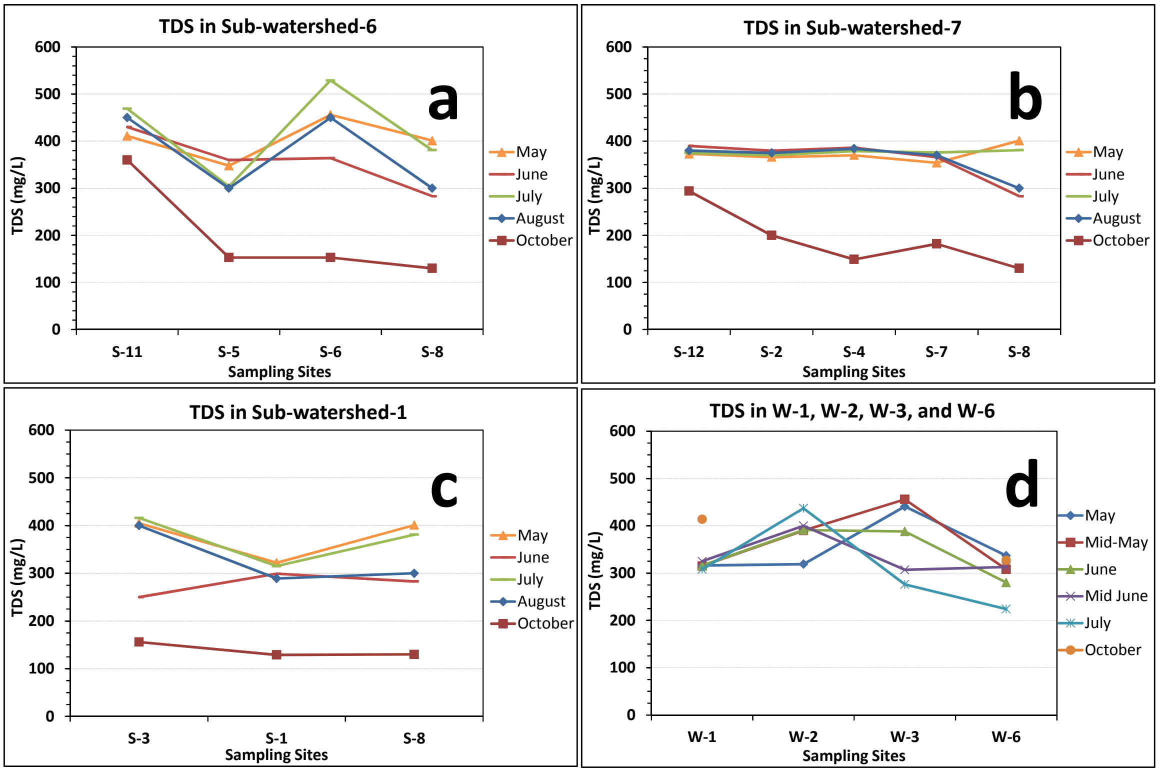


Figure 27. Temporal and spatial variation of TDS in sub-watersheds and wetland.

sources of high TDS (Figure 27 a). These two sites received water either from agricultural lands (S-11) or from both agricultural lands and urban areas (S-6) (Figure 16). Site S-5 or sub-watershed-5 (Figure 20) had low TDS which means that agricultural lands around site S-11 were the major source of TDS in this sub-watershed. Low TDS values in S-5 and S-6 in October (Figure 27 a) could be the effect of dilution. A similar situation (Figure 27 b) was observed in sub-watershed-7 (Figure 21). The major source of TDS was the agricultural lands as S-12, S-2, and S-4 all received water from areas of croplands (Figure 16) and had high TDS (Figure 27 b).

In sub-watershed-1 (Figure 21) the main source of TDS is S-3 (Figure 27 c) which receives water mainly from urban areas (Figure 16). Site S-3 had high TDS as the other high TDS sites like S-11, S-12, and S-4. Site S-1 and S-3 were in the same stream channels but site S-1 showed relatively low TDS (Figure 27). This change happened mainly because there is a wetland in between S-1 and S-3 which reduced TDS from stream water (Figure 27 d). Water from S-3 entered the wetland through W-3 before it reached S-1 (Figure 16). High TDS water entering the wetland from W-2 and W-3 eventually became water with low TDS when it exited the wetland through W-6 (Figure 16 and 27 d).

Stream Discharge

Average stream discharge data from 10 sites are shown in Figure 28. Sites S-11, S-12, S-2, and S-4 were considered upstream sites that are located in agricultural areas (Figure 16). Sites S-3, S-5, S-1, S-6, S-7, and S-8 are further downstream and are located mostly in urban areas (Figure 16). Stream discharge ranged from 3 to 2700 L/sec with the highest discharge recorded at site S-8 in May and the lowest discharge recorded at site S-4 in August. Stream discharge is expected to follow rainfall patterns (Figure 14-15). Accordingly we see high discharge in May, which gradually decreases in the following months in all sites. Site S-8 showed the highest values because it is the outlet point of DRC to the Cedar River (Figure 16). Urban areas have larger amount of surface runoff due to low infiltration for paved surfaces. Therefore, stream discharges in urban sites were relatively high (Figure 28).

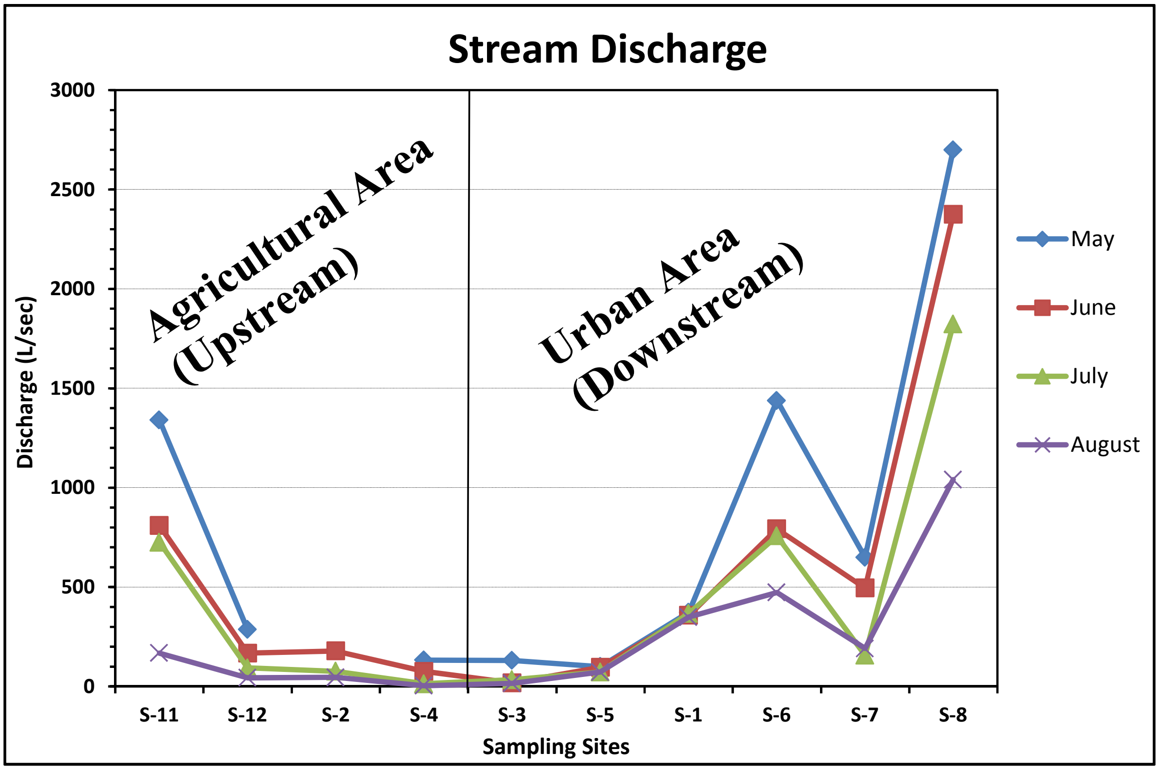


Figure 28. Stream discharge.

<u>In Situ Water Infiltration Rate</u>

Measuring water infiltration rate is important to know the possibility of surface runoff in any specific area. If the precipitation rate exceeds the soil infiltration rate surface runoff will occur if there is no physical barrier. Water infiltration tests were done in the field using the procedure described in Chapter 3. Water infiltration rate was relatively high during the first few minutes of the test after which it gradually decreased. The test was done in the field using simple procedures to compare water infiltration rates in different hydrologic units.

Average water infiltration rates were 7 cm/min (range: 0.7 to 30.0 cm/min) in agricultural lands, 2.9 cm/min (range: 0.8 to 6.4 cm/min) in urban areas, 9.3 cm/min (range: 0.2 to 25.7 cm/min) in stream banks, 1.2 cm/min (range: 0.4 to 2.4 cm/min) in wetland, and 6.8 cm/min (range: 5.5 to 8.0 cm/min) in prairie soils (Figure 29). The agricultural lands had the highest rate among all hydrologic units and the highest range. The sandy sediments at site S-9 also showed high infiltration rate. Sandy sediments in prairie showed higher infiltration rate compared to urban areas (Figure 29). These values are little higher compared to the infiltration rates reported by Black Hawk county soil survey report (USDA, 2013).

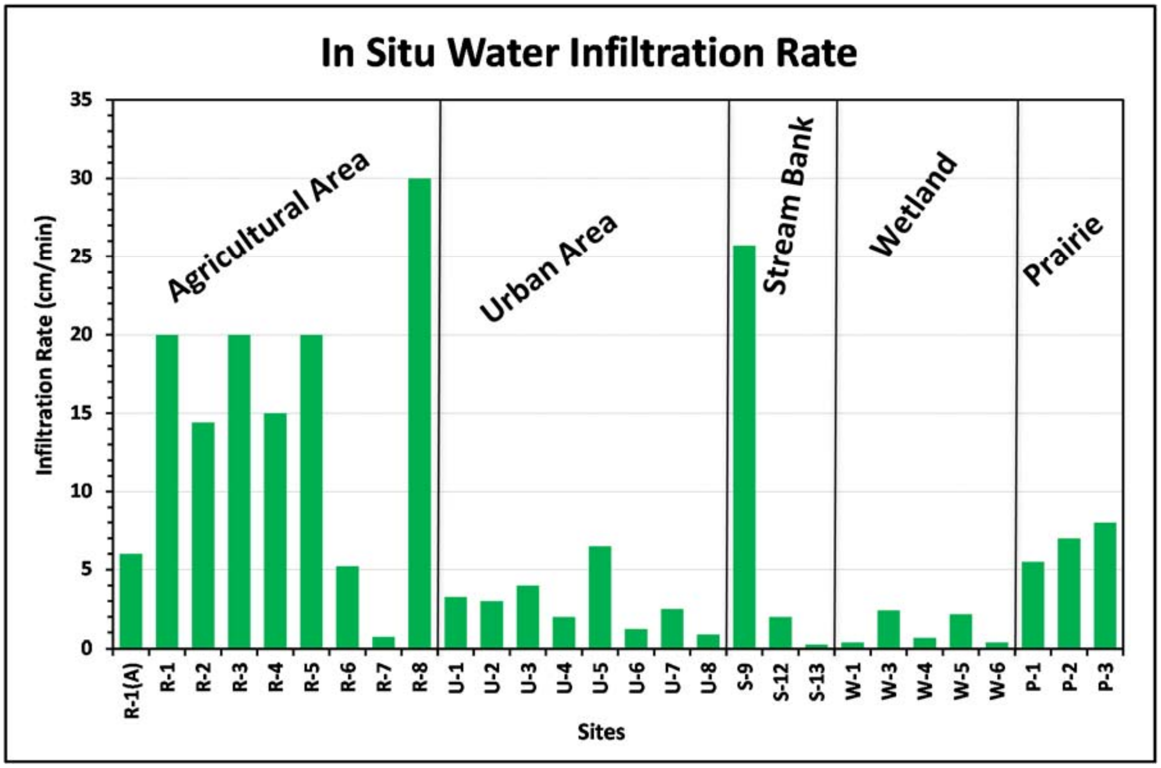


Figure 29. In situ water infiltration rate.

Soil Organic Matter

Agricultural Soil

In agricultural soil, average organic matter (OM) percentages at the surface (0 inch depth) were 8.4 (range: 6.1 to 14.5) in May, 7.2 (range: 5.9 to 8.6) in June, 7.2 (range: 5.7 to 9.3) in July, and 6.9 (range: 5.5 to 8.4) in October. Average OM percentages at a 6 inch depth below the surface were 7.4 (range: 5.4 to 8.9) in May, 6.9 (range: 5.0 to 8.3) in June, 6.8 (range: 5.0 to 10.2) in July, and 6.5 (range: 5.1 to 8.6) in October. Average OM percentages at a 12 inch depth below the surface were 6.7 (range: 5.2 to 7.7) in May, 6.7 (range: 5.0 to 8.9) in June, 6.5 (range: 5.0 to 8.9) in July, and 6.5 (range: 4.2 to 9.5) in October (Figure 30).

Organic matter percentages were relatively higher in May, which gradually decreased toward the end of the growing season in October. At a 12 inch depth profile, OM percentages were low compared to the other depth profiles. Changes in OM percentages were not uniform across the depth profiles (surface, 6 inch, and 12 inch) of the soil. Also, it was not uniform at different sites. Relatively higher change occurred in the surface profile, amounting to more than 17% between May and October. Changes at 6inch depths were around 12 % for the same time period (Figure 30).

Urban Soil

In urban soil, average organic matter percentages at the surface (0 inch depth) were 7.5 (range: 4.0 to 11.3) in May, 10.7 (range: 5.6 to 11.7) in June, 7.2 (range: 4.8 to 10.8) in July, and 6.5 (range: 4.2 to 9.9) in October. Average OM percentages at 6 inch depth below surface were 5.3 (range: 3.1 to 7.9) in May, 7.1 (range: 5 to 7.2) in June,

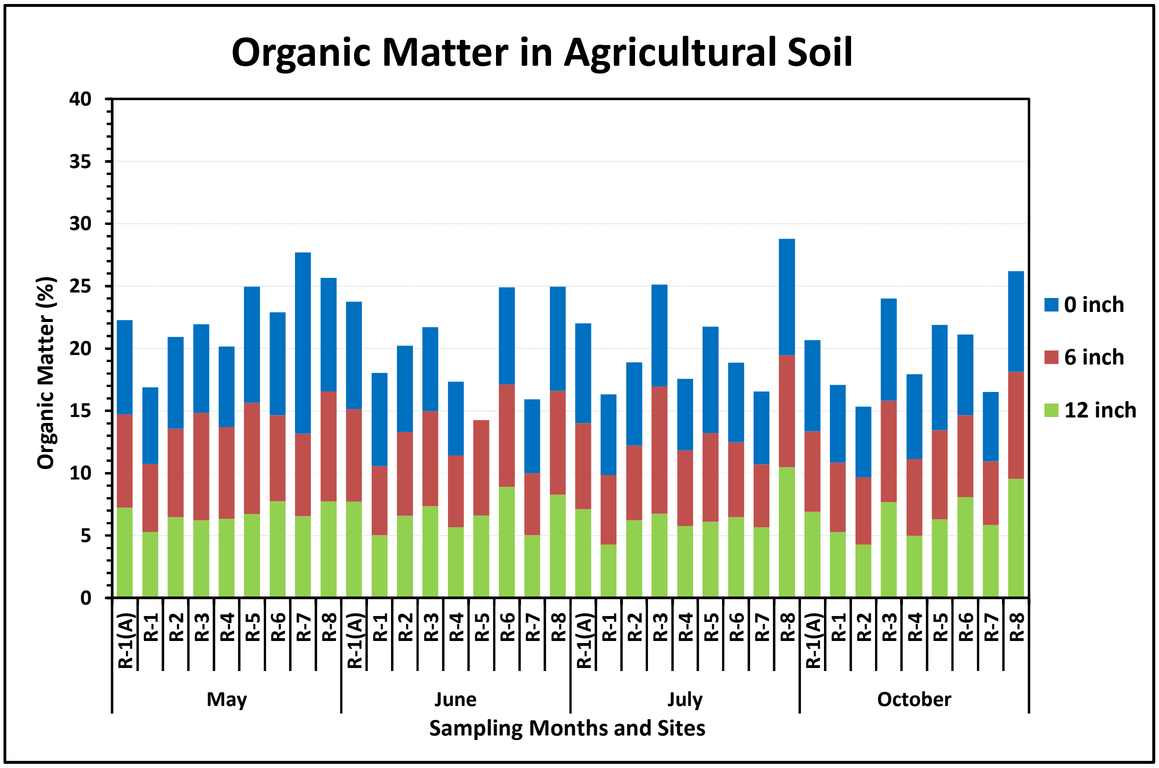


Figure 30. Organic matter percentage in agricultural soil.

6.3 (range: 4.5 to 10.2) in July, and 5.4 (range: 3.6 to 9.2) in October. Average OM percentages at 12 inch depth below surface were 4.9 (range: 3.2 to 9.8) in May, 6.5 (range: 4.3 to 10.1) in June, 6.1 (range: 4.4 to 10) in July, and 5.7 (range: 4 to 8.3) in October (Figure 31).

Organic matter percentages were relatively higher in May, and gradually decreased towards the end of the growing season in October. At the 12 inch depth profile, OM percentages were lower compared to the other depth profiles. Changes in OM percentages were not uniform across the depth profiles (surface, 6 inch, and 12 inch) of the soil. Also, it was not uniform at different sites. Relatively higher change occurred in

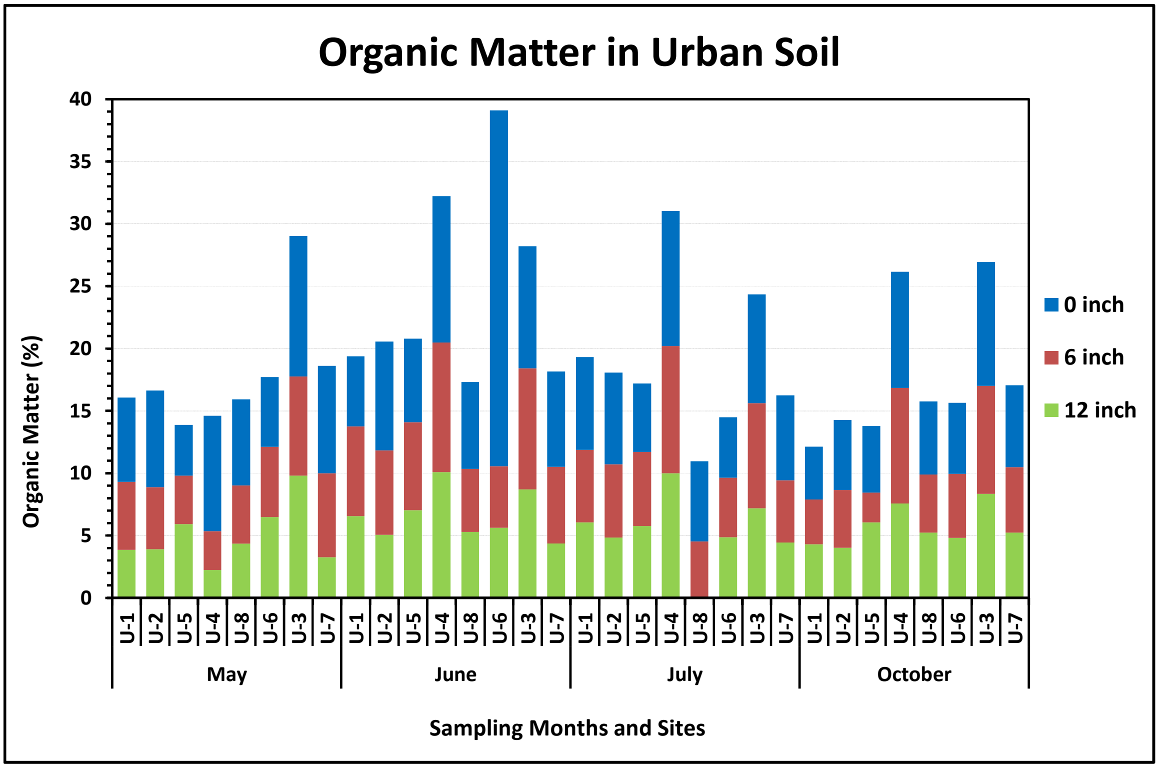


Figure 31. Organic matter percentage in urban soil.

surface profiles, amounting to about 12.6% between May and October. Change in 12 inch depth profile was about 16 % and at 6 inch depth change was insignificant for the same time period (Figure 31).

Stream Bank Soil

In stream bank soil, average organic matter percentages at the surface (0 inch depth) were 6.1 (range: 3.2 to 8.7) in May, 5.8 (range: 2.1 to 7.6) in June, 5.6 (range: 1.9 to 8.2) in July, and 4.9 (range: 2.1 to 8.5) in October. Average OM percentages at a 6 inch depth below surface were 5.2 (range: 1.7 to 7.5) in May, 4.7 (range: 2.7 to 6.7) in June, 4.8 (range: 1.3 to 7.5) in July, and 4.1 (range: 1.3 to 7.4) in October. Average OM percentages at 12 inch depth below surface were 5.3 (range: 1.3 to 8.6) in May, 5.0 (range: 3.6 to 6.7) in June, 4.4 (range: 2.6 to 6.9) in July, and 4.5 (range: 1.5 to 6.9) in October (Figure 32).

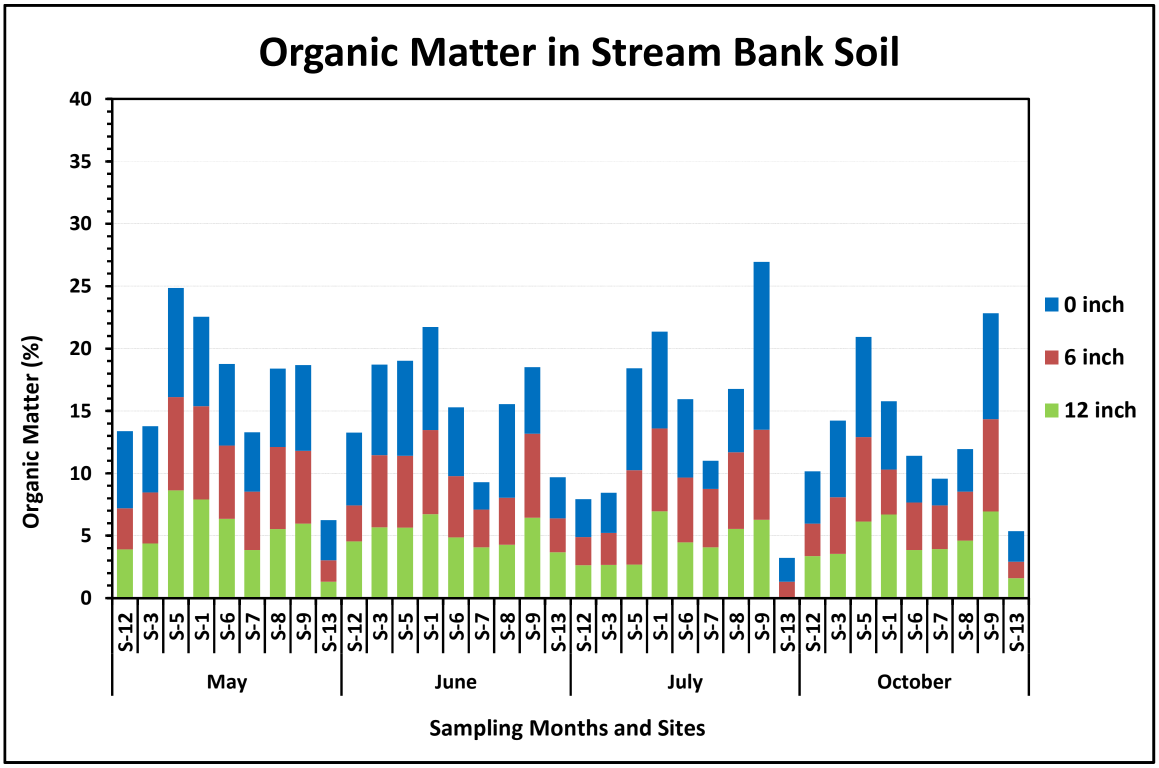


Figure 32. Organic matter percentage in stream bank soil.

Organic matter percentages were relatively higher in May, which gradually decreased toward the end of the growing season in October. At 12 inch depth profile, OM percentages were lower compared to the other depth profiles. Changes in OM percentages were not uniform in across the depth profiles (surface, 6 inch, and 12 inch) of the soil. Also, it was not uniform at different sites. Relatively higher change occurred in surface profiles, amounting to more than 20% between May and October. Changes at other depths were around 15 % for the same time period (Figure 32).

Wetland Soil

In wetland soil, average organic matter percentages at the surface (0 inch depth) were 4.8, 2.8, 4.9, and 4.2 in May, June, July and October, respectively. Average OM percentages at a 6 inch depth below surface were 3.4, 2.2, 2.5, and 2.8 in May, June, July, and October respectively. Average OM percentages at 12 inch depth below surface were 3.4, 1.5, 1.8, and 2.0 in May, June, July, and October respectively (Figure 33).

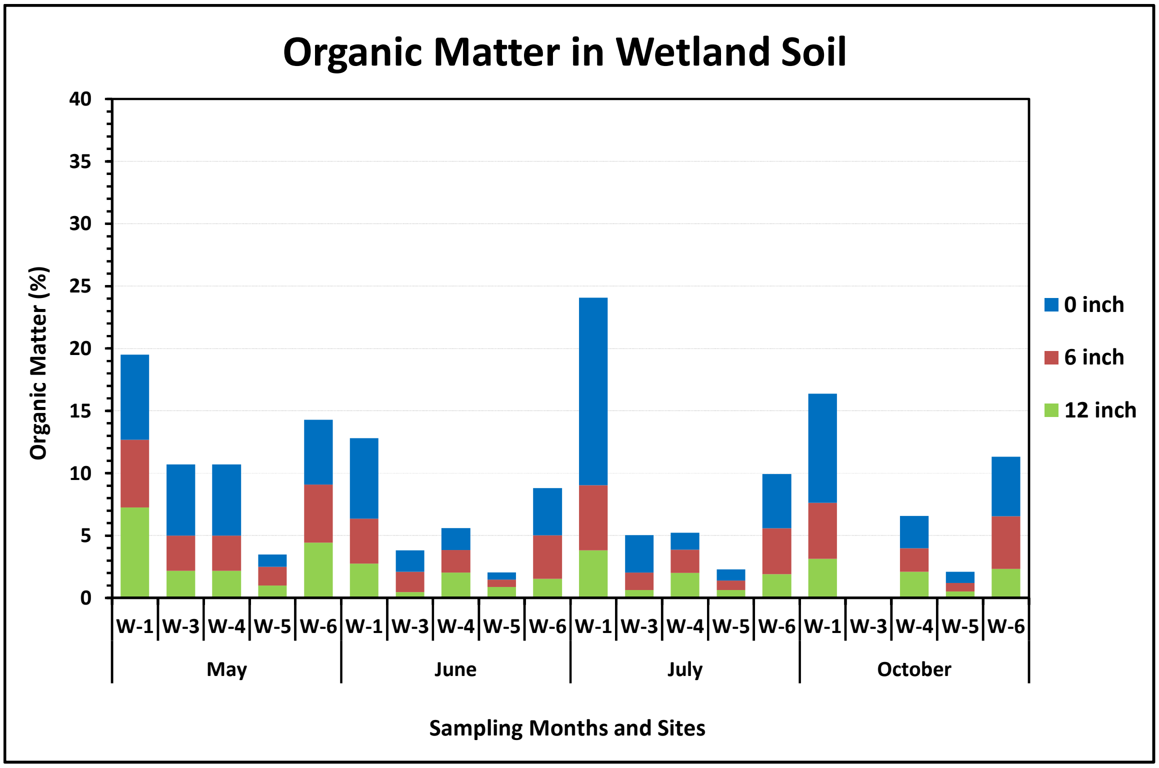


Figure 33. Organic matter percentage in wetland soil.

Organic matter percentages were relatively higher in the southeastern part (W-1 and W-6) of the wetland (Figure 16 and 33). This may be due to the restoration activity to improve the wetland capacity that removed surface soils from the center of the wetland. Organic matter percentages were relatively higher in May and it gradually decreased towards the end of the growing season in October. At 12 inch depths OM percentages were relatively lower compared to the other depth profiles. Changes in OM percentages were not uniform across the depth profiles (surface, 6 inch, and 12 inch) of the soil. Also, it was not uniform at different sites. Relatively higher change occurred in 12 inch depth profiles, amounting to more than 40.8% between May and October. Changes at other depths were around 17.5 % for the same time period (Figure 33).

Prairie Soil

In prairie soil, average organic matter percentages at the surface (0 inch depth) were 9.0, 5.7, and 9.4 in May, June, and October, respectively. Average OM percentages at a 6 inch depth below surface were 8.7, 3.8, and 4.4 in May, June, and October respectively. Average OM percentages at 12 inch depth below surface were 3.6, 3.2, and 3.0 in May, June, and October, respectively (Figure 34).

In terms of organic matter, all hydrologic units showed similar types of aerial and vertical distribution throughout the study period (Figure 30-34). More than 95% of the samples showed over 4% organic matter in the soil, this was expected in the Midwest regions of the US (USDA, 2013). Agricultural areas showed the highest overall OM percentages and wetland areas had the lowest OM percentages. Urban areas also had high OM percentages as most of those areas were either agricultural land or wetland or prairies

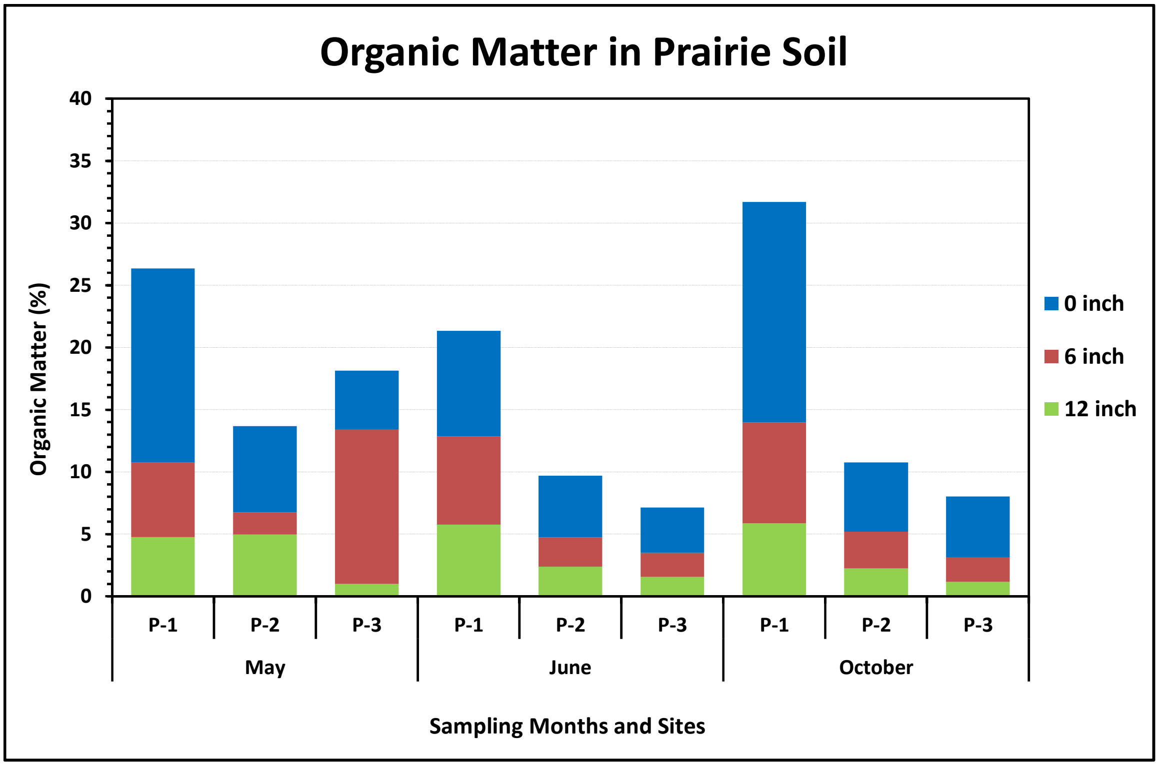


Figure 34. Organic matter percentages in prairie soil.

before being converted to residential areas a few years ago. The wetland in the study area was a constructed wetland. Top soil of the wetland was removed during its construction, which resulted in OM percentages being relatively low. The Cedar Hills Sand Prairie sediments were mostly sandy and the observed OM percentages were also low as expected.

Nitrate

Nitrogen as nitrate (NO_3^-) is common both in groundwater and surface water (Freeze and Cherry, 1979). Nitrate is very mobile in the hydrologic system and can move with groundwater with little or no retardation or transformation (Freeze and Cherry, 1979). Nitrate in water can come from fertilizer runoff from croplands, lawns, and golf courses; decomposition of soil organic matter, human and animal wastes; and industrial wastes, municipal landfills and mining activities. However, evidence suggests that agriculture, through the use of inorganic fertilizers, is the major contributor (Hallberg et al., 1985). In this study, the analyte was measured as nitrate (NO_3^-). According to U.S. EPA, the MCL of dissolved N is 45 mg/l as nitrate (NO_3^-) for public drinking water (U.S. EPA, 2013 b).

Soil nitrate was extracted by using deionized (DI) water. To compare this method with other standard methods several samples were extracted using both distilled water and 2M KCl solution. Table 1 shows the comparison of soil nitrate concentration extracted by two different methods. For this comparison, samples were taken from all depth profiles and from different hydrologic units. Samples from all types of soils were used for this comparison. Comparison clearly shows that DI water is an acceptable extractor of soil nitrate. In several cases DI water proven better than KCl (Table 1).

Nitrate in Agricultural Soil

In agricultural soil, average nitrate concentration in surface (0 inch depth) soil was 97 mg/kg (range: below detection to 436 mg/kg) in May, 42 mg/kg (range: below detection to 156 mg/kg) in June, 172 mg/kg (range: 62 to 526 mg/kg) in July, and 114 mg/kg (range: 38 to 213 mg/kg) in October. At 6 inch depth, average soil nitrate concentration was 40 mg/kg (range: below detection to 207 mg/kg) in May, 74 mg/kg (range: 45 to 203 mg/kg) in June, 78 mg/kg (range: 34 to 184 mg/kg) in July, and 61 mg/kg (range: below detection to 158 mg/kg) in October. At 12 inch depth, average soil

Table-1. Comparison between two soil nitrate extraction methods.

		Extracted water's nitrate concentration (mg/l)	
Sample ID	Depth (in)	With DI water	With 2M KCL
P-1	0	1.08	n.a.
P-2	6	n.a.	n.a.
P-3	12	n.a.	n.a.
R-1	0	1.09	n.a.
R-2	6	1.98	n.a.
R-3	0	5.22	n.a.
U-2	12	n.a.	n.a.
U-3	0	n.a.	n.a.
U-6	6	n.a.	n.a.
S-1	0	1.54	n.a.
S-4	0	1.72	n.a.
S-12	0	1.19	n.a.

*n.a means below machine's detection limit.

nitrate concentration was 51 mg/kg (range: below detection to 290 mg/kg) in May, 35 mg/kg (range: below detection to 73 mg/kg) in June, 51 mg/kg (range: below detection to 106 mg/kg) in July, and 47 mg/kg (range: below detection to 193 mg/kg) in October (Figure 35).

Soil nitrate concentration was the lowest in May (except R-3) and gradually increased in the months of June and July and then decreased in October (Figure 35). Nitrate concentration in May represented soil nitrate before the beginning of growing season and nitrate concentration in October represented soil nitrate after the growing season when there were no more agricultural activities. Agricultural soil had no significant change in OM percentages within the growing season (Figure 32). There were

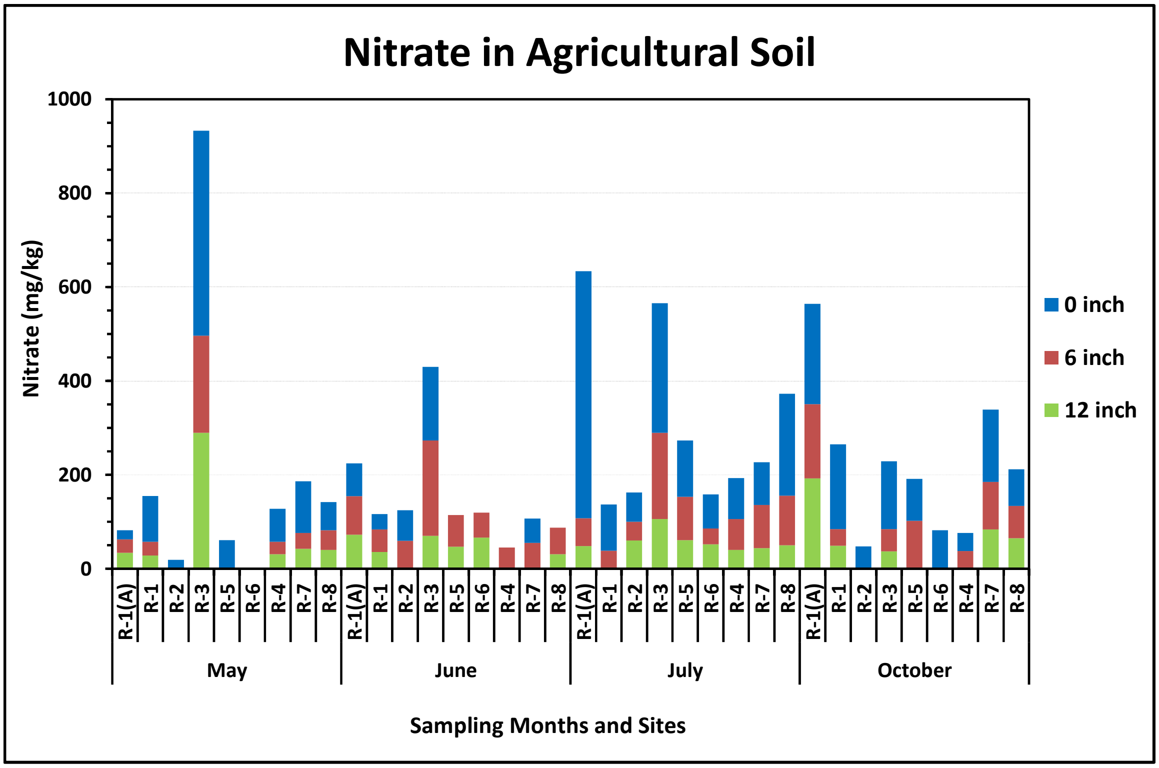


Figure 35. Soil nitrate concentration in agricultural soil.

no significant industrial or municipal waste management activities in the agricultural area. Given that atmospheric nitrogen deposition is insignificant, the main source of nitrate in the soil was either the inorganic fertilizers or the manure fertilization used in crop production.

Almost in every site, soil nitrate concentration increased at depth profiles of 6 and 12 inches after May (Figure 35). Surface nitrate concentration in June was low compared to the other months. This may be due to the dilution through early May rain events (Figure 14) and plant uptake of nitrogen as initially the plant roots were not deep and they used available nitrate from the surface. Also, the dry weather might have increased denitrification through ammonia volatilization and eventually lowered the surface nitrate concentration. In some sites (R-1A, R-2, and R-6) the total soil nitrate (sum of soil nitrate from all depth profiles) had increased due to the increase of nitrate in each depth profile. In other sites, (R-4, R-5, R-7, and R-8) the total soil nitrate either went up or down along with the increase of soil nitrate in 6 and/or 12 inch depth (Figure 35). Thus, the general increase of nitrate concentration at 6 and 12 inch depths in successive months indicates downward infiltration of nitrate.

Nitrate in Urban Soil

In urban soils, average nitrate concentration in surface (0 inch depth) soil was 20 mg/kg (range: below detection level to 48 mg/kg) in May, 20 mg/kg (range: below detection level to 47 mg/kg) in June, 62 mg/kg (range: below detection to 105 mg/kg) in July, and 42 mg/kg (range: below detection to 190 mg/kg) in October. At 6 inch depth, average soil nitrate concentration was 22 mg/kg (range: below detection to 64 mg/kg) in May, 9 mg/kg (range: below detection to 43 mg/kg) in June, 42 mg/kg (range: below detection to 82 mg/kg) in July, and 11 mg/kg (range: below detection to 52 mg/kg) in October. At 12 inch depth, average soil nitrate concentration was 11 mg/kg (range: below detection to 31 mg/kg) in May, below detection in June, 24 mg/kg (range: below detection to 52 mg/kg) in July, and 11 mg/kg (range: below detection to 47 mg/kg) in October (Figure 36).

Soil nitrate in urban areas was the lowest during June and the highest in July. Observed changes in OM percentages within the study period were insignificant (Figure 31). There were no significant industrial or municipal waste management activities in the

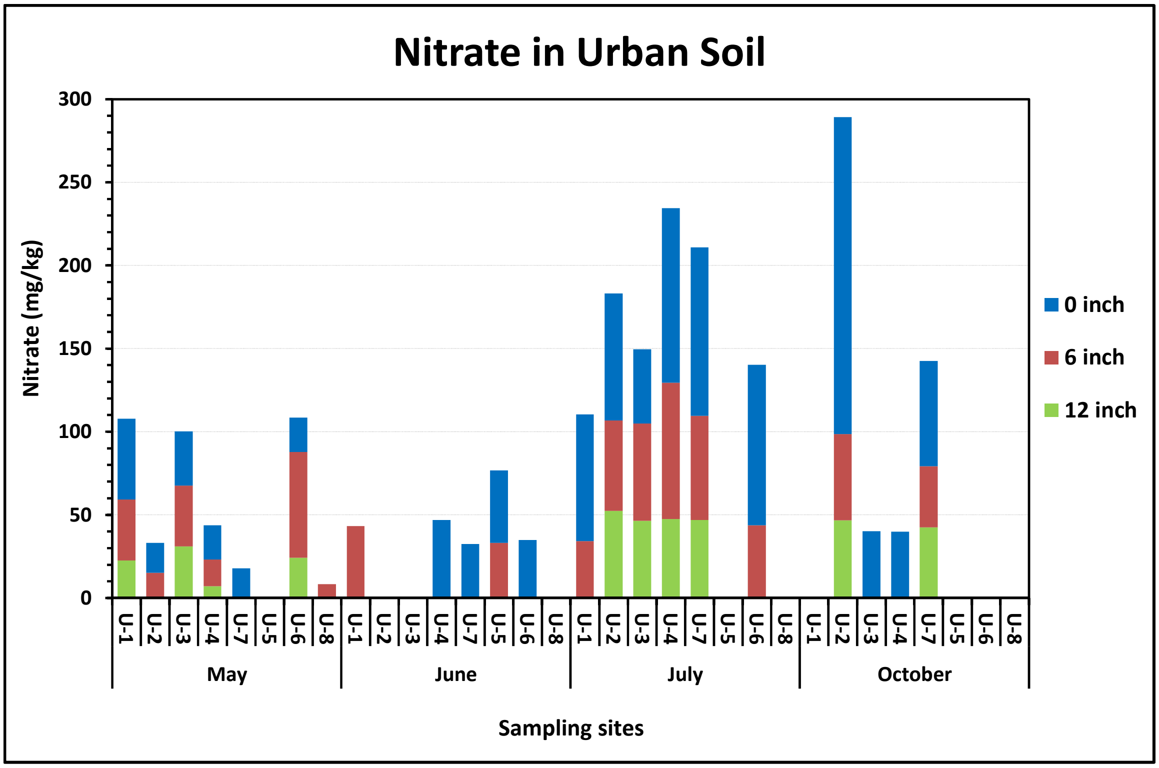


Figure 36. Nitrate in urban soil.

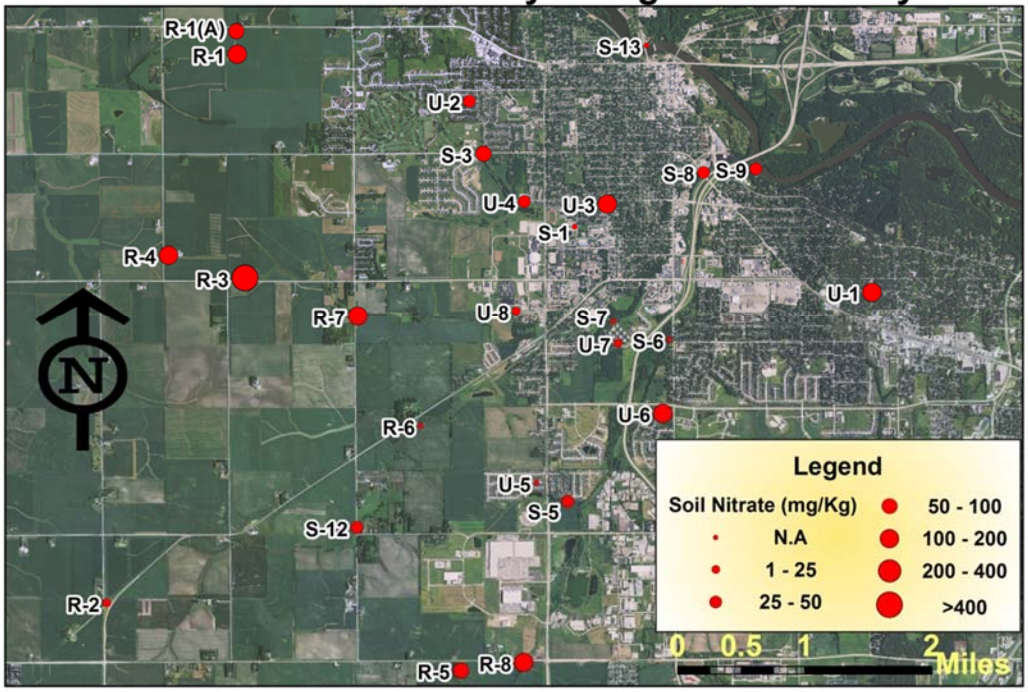
urban area. Also, atmospheric deposition of nitrogen is known to be insignificant. Therefore, the main source of nitrate in the soil was inorganic fertilizer used in lawns.

There were a few rain events in early May after the May sampling of soil. But there were no significant rain events from the middle of May to the end of June (Figure 14). Denitrification, dilution from early May rain, and no use of additional fertilizer during the dry period combined might be the cause of the lowest nitrate concentration in June. Amonium nitrate and andydrous ammonia are the most commonly used fertilizers in Iowa. Thus, sudden peaks and random high nitrate at different sites might be the result of frequent and random use of lawn fertilizers in urban areas. There were few rain events in July, August and September (Figure 14 and 15) which might have released and washed out nitrate from soil. Therefore, soil nitrate concentration in October is low compared to that in July.

In most sites, the soil nitrate concentration decreased at all depth profiles from May to June (Figure 36). Surface nitrate was high compared to other depth profiles during the study period. This was due to the use of lawn fertilizers on the surface. At most sites (U-1 to U-4, U-6, and U-7), nitrate concentration in 6 and 12 inch depth profiles increased from June to July along with the total nitrate concentration. But in October, four (U-1, U-3, U-4, and U-6) of the six sites had soil nitrate below detection level at 6 and 12 inch depths (Figure 36). Thus, the initial increase followed by a decrease in nitrate concentration at 6 and 12 inch depths in successive months indicates downward infiltration of nitrate.

Urban areas within the DRC watershed are mainly residential areas (Figure 16). Some sampling sites were chosen from the middle of the urban area, away from the stream channels (U-1 to U-4, and U-7). Other sites were chosen from the edge of the urban area, close to stream channels (U-5, U-6, and U-8) (Figure 16). Sites chosen from the middle of the residential area (U-1 to U-4, and U-7) showed high total soil nitrate as well as the surface nitrate compared to the sites chosen from the edge of the urban area (U-5, U-6, and U-8) (Figure 36-38). Sites located in the middle of the residential area appear to have received high lawn fertilizers from the surrounding areas. This indicates a measurable influence of lawn fertilizer on the soil nitrate concentration. On the other hand, sites from the edge of the urban area had low total nitrate as well as low nitrate at 6

Soil Nitrate in Different Hydrologic Units in May



Soil Nitrate in Different Hydrologic Units in June

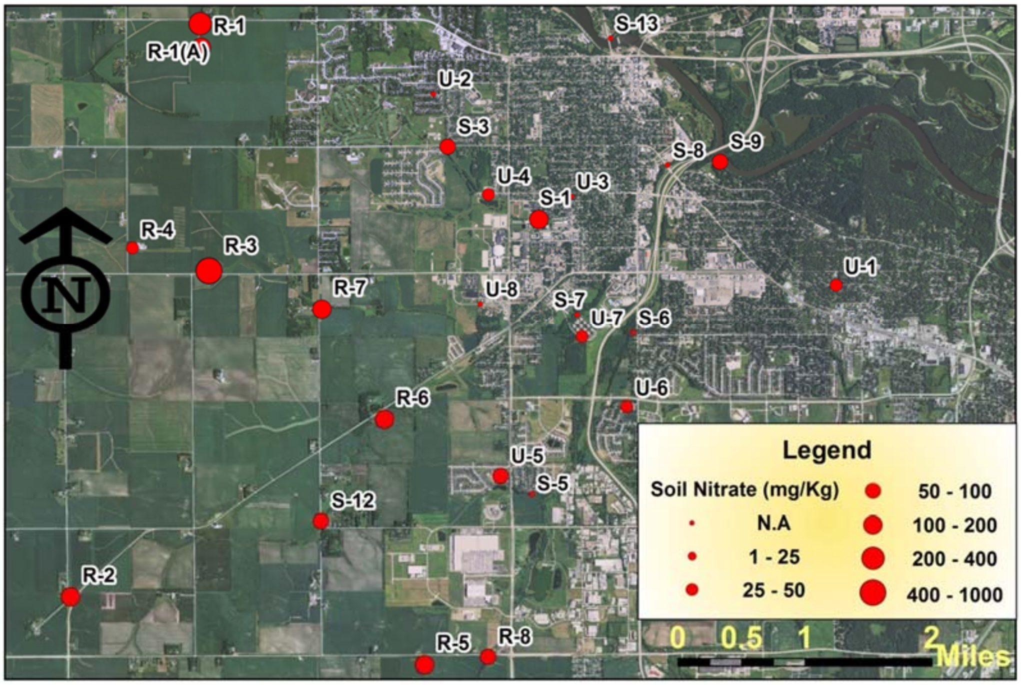
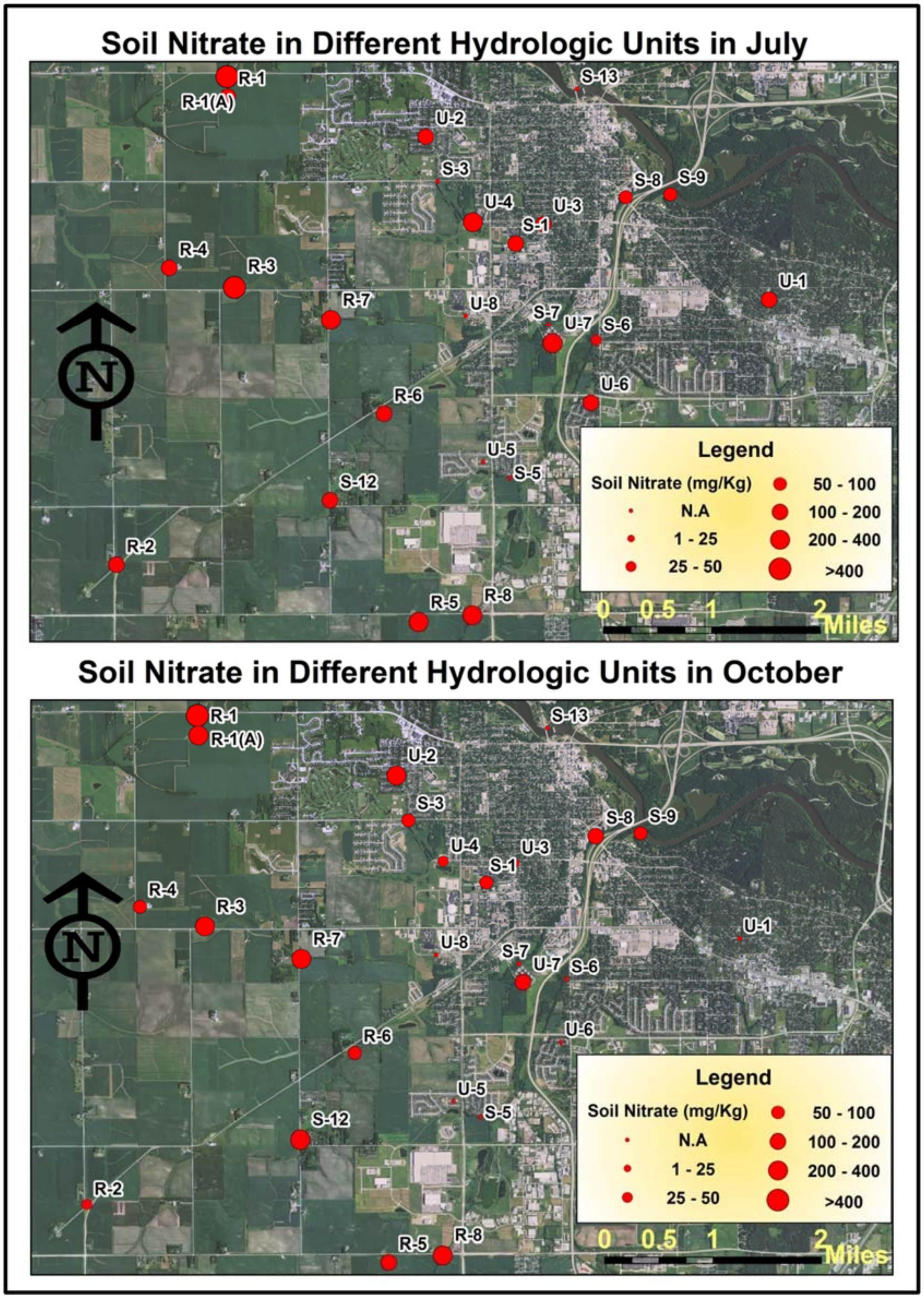


Figure 37. Spatial map of total soil nitrate (all depth profiles) in different hydrologic units in May and June.



Soil Nitrate in Different Hydrologic Units in July

Soil Nitrate in Different Hydrologic Units in October

Figure 38. Spatial map of total soil nitrate (all depth profiles) in different hydrologic units in July and October.

and 12 inch depths compared to sites from the middle of the residential areas (Figure 36-38). Sites close to the stream channels are the least impacted by fertilizers from the surrounding areas. Besides, these sites have active base flow causing N removal from soil compared to the sites from the middle of the residential areas.

Nitrate in Stream Bank Soil

In stream bank soil, average nitrate concentration in surface (0 inch depth) soil was 12 mg/kg (range: below detection level to 38 mg/kg) in May, 14 mg/kg (range: below detection level to 48 mg/kg) in June, 29 mg/kg (range: below detection to 105 mg/kg) in July, and 31 mg/kg (range: below detection to 127 mg/kg) in October. At 6 inch depth, average soil nitrate concentration was 7 mg/kg (range: below detection to 32 mg/kg) in May, 16 mg/kg (range: below detection to 67 mg/kg) in June, 10 mg/kg (range: below detection to 44 mg/kg) in July, and 14 mg/kg (range: below detection to 50 mg/kg) in October. At 12 inch depth, average soil nitrate concentration was 4 mg/kg (range: below detection to 33 mg/kg) in May, 10 mg/kg (range: below detection to 46 mg/kg) in June, 9 mg/kg (range: below detection to 44 mg/kg) in July, and 18 mg/kg (range: below detection to 64 mg/kg) in October (Figure 39).

Soil nitrate in stream bank soils was the lowest in May, and increased in the following months (Figure 39). Observed changes in OM percentages within the study period were insignificant (Figure 32). There were no significant industrial or municipal waste management activities in the DRC watershed area. Also, the amount of atmospheric nitrogen deposition is insignificant. Therefore, the main source of nitrate in the stream bank soil was inorganic fertilizer used in agricultural lands and lawns in urban

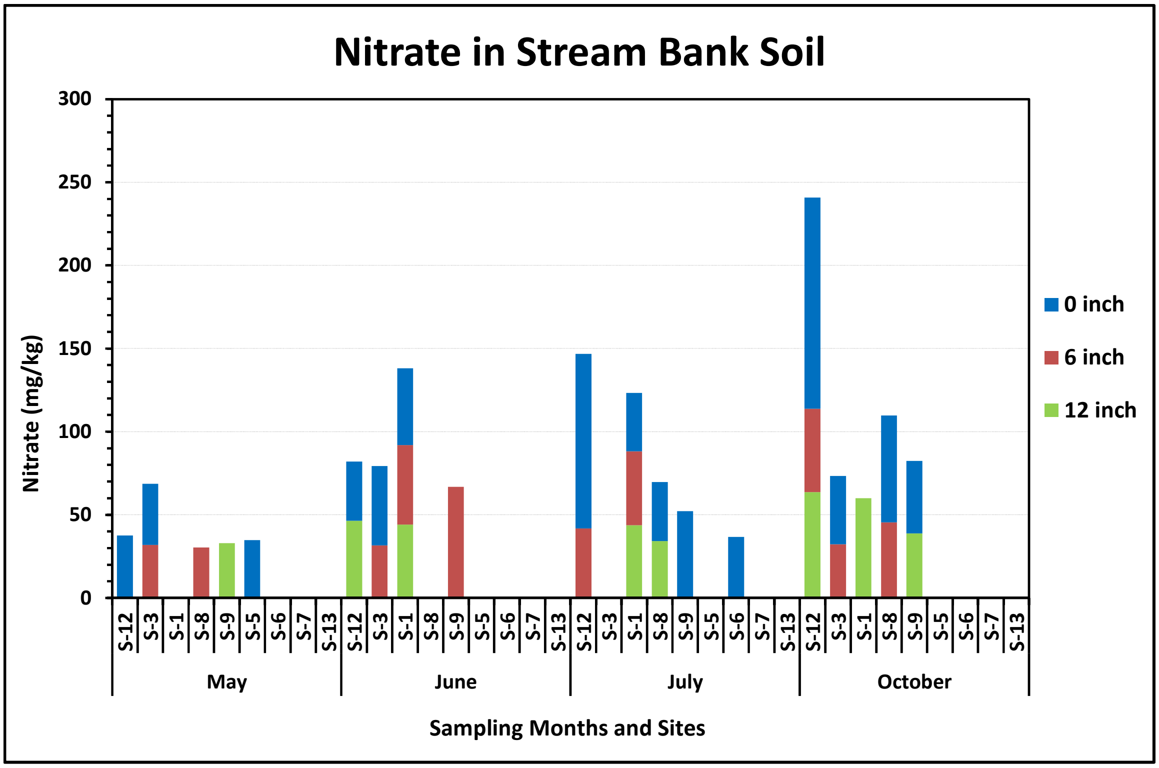


Figure 39. Nitrate in stream bank soil.

areas. There were a few rain events in early May after the May sampling of soil, but there were no significant rain events from the middle of May to the end of June (Figure 14). Converging runoff and base flow caused by the rain events might have brought excess nitrate from the surrounding areas and increased the level of nitrate in June and thereafter.

During the study period, nitrate concentration varied within the sites (S-12, S-1, S-8, and S-9) at different depth profiles with the increase or decrease of total nitrate amount (Figure 39). Stream bank sediments had no direct nitrogen sources, but they received nitrate from other hydrologic units. Thus, these fluctuations indicate active movement of nitrogen within the DRC watershed, both vertically and spatially.

Sites (S-1, S-3, S-5 to S-9, and S-13) chosen in or around urban areas had lower nitrate concentration compared to the site (S-12) close to the agricultural land (Figure 37-39). Sites located along the edge of the urban areas (S-5 to S-7 and S-13) didn’t show any nitrate, except at S-5 in May (at 0 inch) and at S-6 in July (at 0 inch) (Figure 37-39). Two downstream sites (S-8 and S-9) had generally high nitrate concentrations at 6 and 12 inch depths (Figure 37-39). These sites are located where DRC meets with Cedar River (Figure 37 and 38). Therefore, these sites might have received nitrate through base flow from the upstream areas.

Nitrate in Prairie

Soil samples from the Cedar Hills Sand Prairie didn’t have any nitrate except in June (Figure 40). The concentrations in June samples were below 80 mg/kg, which is attributed to the nitrogen fixed by prairie vegetation and microorganisms.

Nitrate in Surface Water

In stream water, average nitrate concentration was 39 mg/l (range: 2 to 88 mg/l) in May, 29 mg/l (range: 2 to 80 mg/l) in June, 8 mg/l (range: 2 to 20 mg/l) in July, 8 mg/l (range: 8 to 4 mg/l) in August, and 4 mg/l (range: 1 to 11 mg/l) in October (Figure 41). Most sites had high concentrations in May and June, then suddenly dropped in July and remained low in the following months (Figure 41). This can be linked to the nitrogen fertilizers and manure application in agricultural fields. Manures are routinely applied to

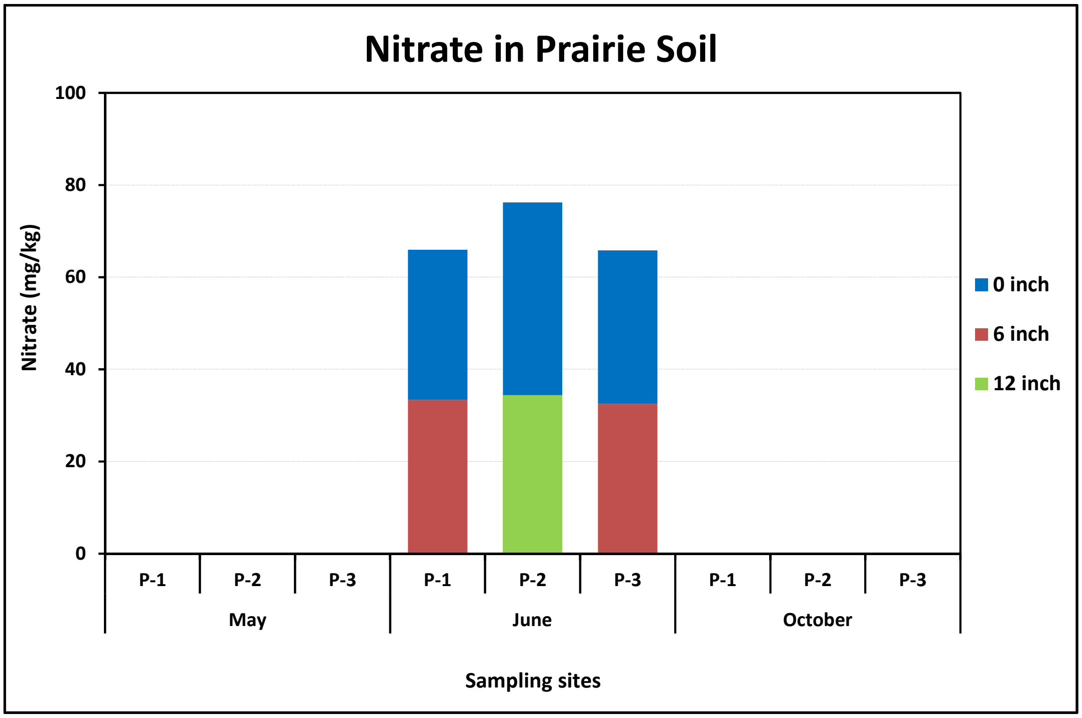


Figure 40. Nitrate in prairie soil.

the fields in late spring, whereas chemical fertilizers are applied between late spring and early summer.

All of the upstream sites in the watershed are located in agricultural lands (Figure 16). These sites (S-2, S-4, S-12, and S-11) had higher nitrate concentrations compared to the other sites located within and around the urban areas (Figure 41- 43). Nitrate concentrations at these sites exceeded 40 mg/l in May and June. The rest of the sites had nitrate concentrations around 20 mg/l or less during these two months. After June, all sites had nitrate at or below 10 mg/l.

Figure 44 shows the nitrate concentration in different sub-watersheds of DRC and the Cedar River (Figure 20 and 21). In sub-watershed-6 (Figure 44 a), the main source of

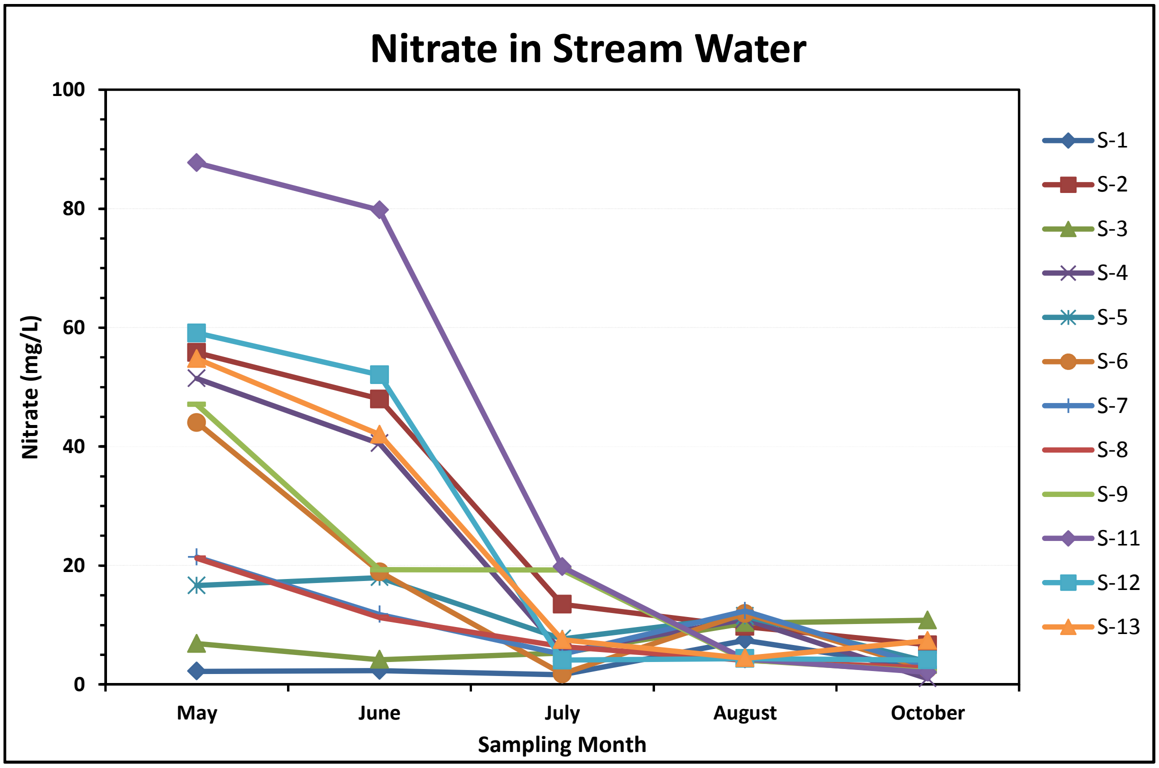
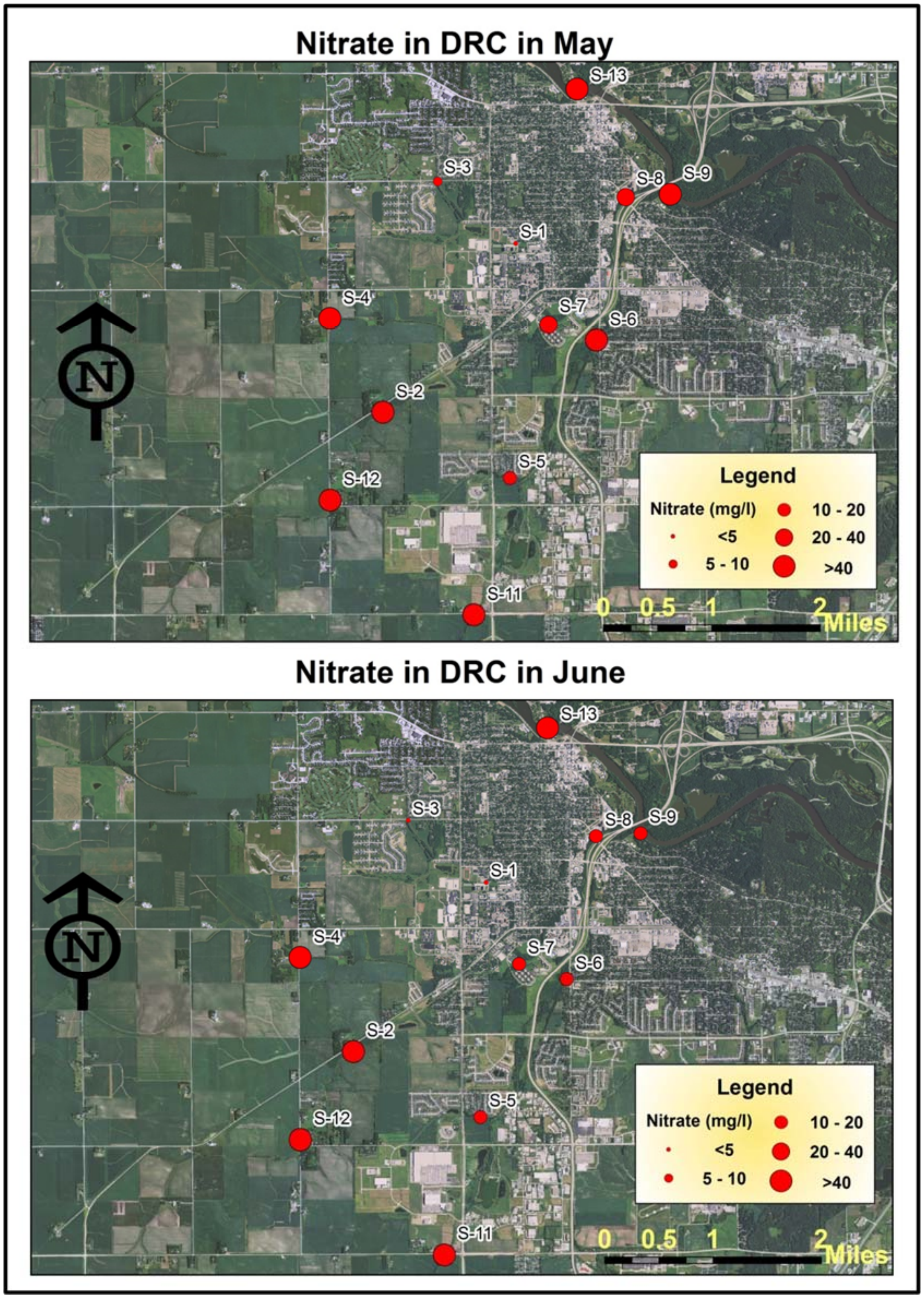


Figure 41. Nitrate in stream water.

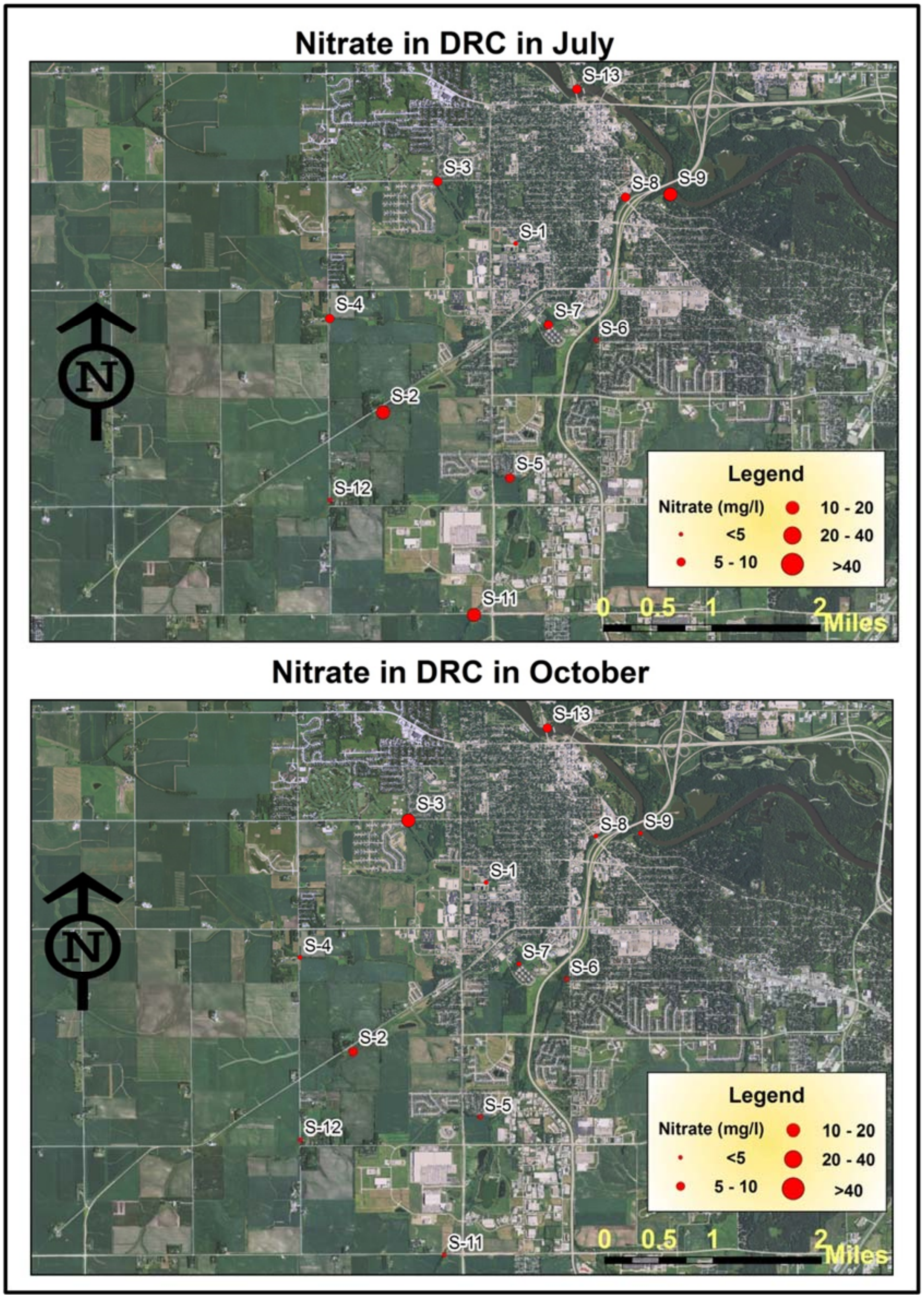
nitrate is site S-11, located in an agricultural area (Figure 42 and 43). Site S-6, which is located along the edge of the urban areas (Figure 42 and 43), is also contributing significant amount of nitrate.

In sub-watershed-7 (Figure 44 b), the main sources of nitrate are sites S-12, S-2, and S-4. These three sites are also located in agricultural areas (Figure 42 and 43). In sub-watershed-1 (Figure 44 c), nitrate concentration is relatively low compared to other sub-watersheds. In sub-watersheds-6 and 7, levels of dissolved nitrate decreased as the main channels approached the urban areas (Figure 42-44). This might be the effect of dilution as these channels received surface runoff from urban areas that had low levels of nitrate


Nitrate in DRC in May

Nitrate in DRC in June

Figure 42. Spatial map of nitrate in stream water (DRC) in May and June.



Nitrate in DRC in July

Nitrate in DRC in October

Figure 43. Spatial map of nitrate in stream water (DRC) in July and October.

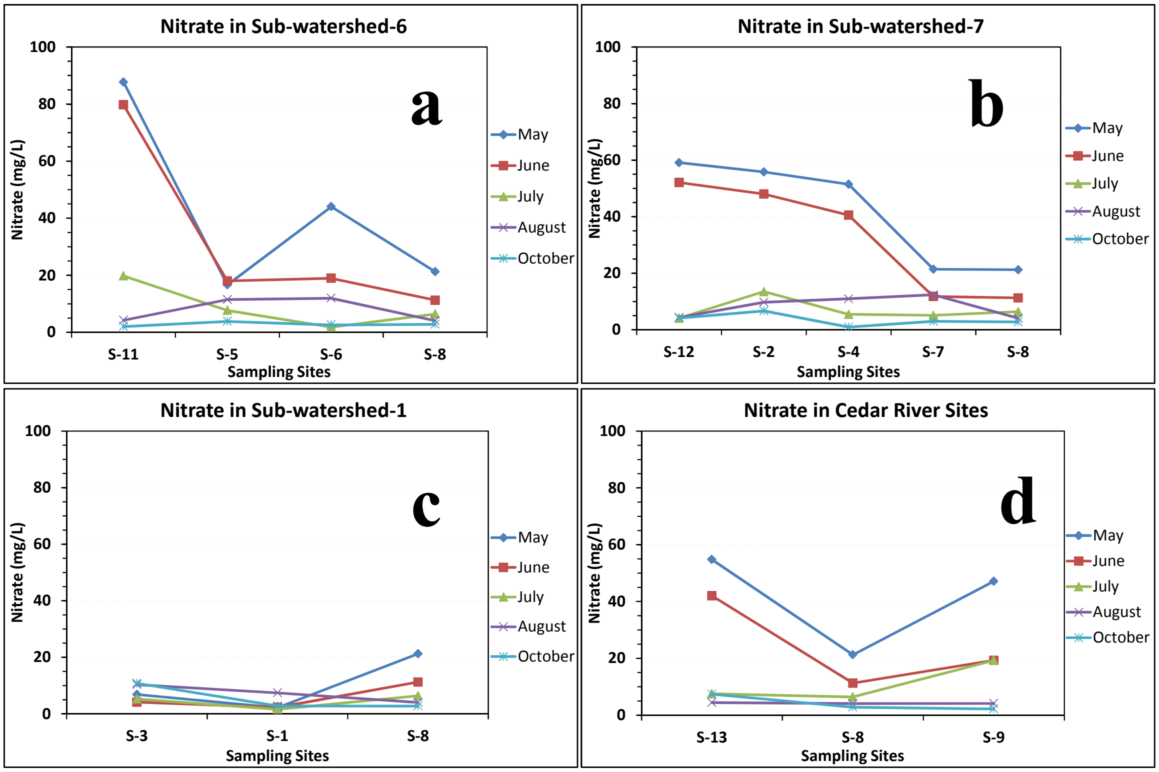


Figure 44. Nitrate in different sub-watersheds of DRC and Cedar River.

dissolved compared to the agricultural areas. Due to this dilution, even though the upstream areas of the sub-watersheds had high nitrate, the concentration dropped when they all approached the site S-8 (Figure 42-44). As a result, even though upstream sites of DRC had higher N concentrations compared to the Cedar River, the level of nitrate appeared high in Cedar River compared to DRC at site S-8 (Figure 44 d). Average nitrate concentration was within the range of what Shrestha (2008) reported for DRC and IOWATER (2010) for Iowa surface water bodies.

In wetland water, average nitrate concentration was 5 mg/l (range: below detection to 15 mg/l) in May, 2 mg/l (range: below detection to 12 mg/l) in June, 2 mg/l (range: below detection to 6 mg/l) in July, and no nitrate was found in October

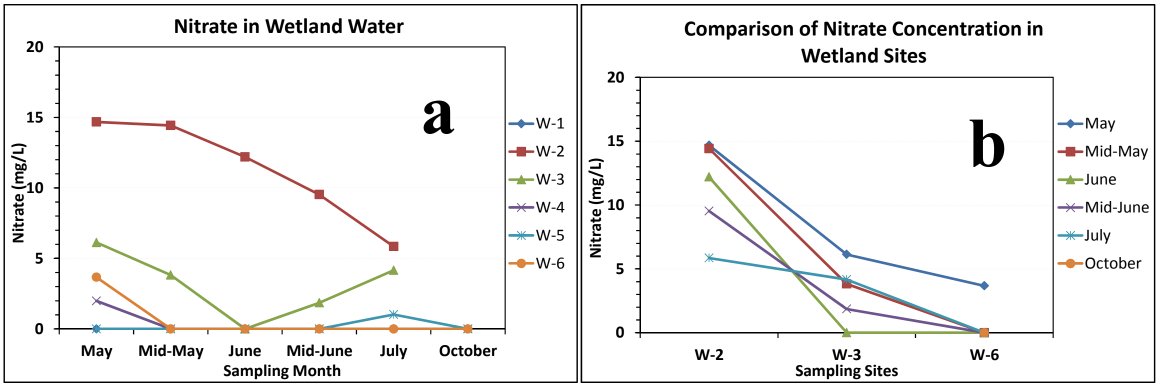


Figure 45. Nitrate in wetland water.

(Figure 45 a). The highest nitrate concentration was observed in May, then gradually decreased thereafter. Site W-2 had the highest concentration and site W-6 had the lowest. Relatively low nitrate in site W-3 and W-4 is attributed to the surrounding urban areas. Though some of the inlet points (W-2 and W-3) had nitrate in water, the outlet point (W-6) didn't show any nitrate (Figure 45 b). It is a good indication that the wetland is uptaking nitrate from water.

Nitrate in Groundwater

In urban wells, average nitrate concentration was 13 mg/l (range: below detection to 40 mg/l) in May, 14 mg/l (range: below detection to 41 mg/l) in June, and 15 mg/l (range: below detection to 41 mg/l) in July (Figure 46 a). In agricultural wells, average nitrate concentration was 5 mg/l (range: below detection to 11 mg/l) in May, 2 mg/l (range: below detection to 6 mg/l) in June, and 6 mg/l (range: below detection to 14 mg/l) in July, and 5 mg/l (range: below detection to 15 mg/l) in October (Figure 46 b).

Nitrate concentrations in urban wells were high compared to agricultural wells. During the study period, nitrate concentration in groundwater didn't change temporally

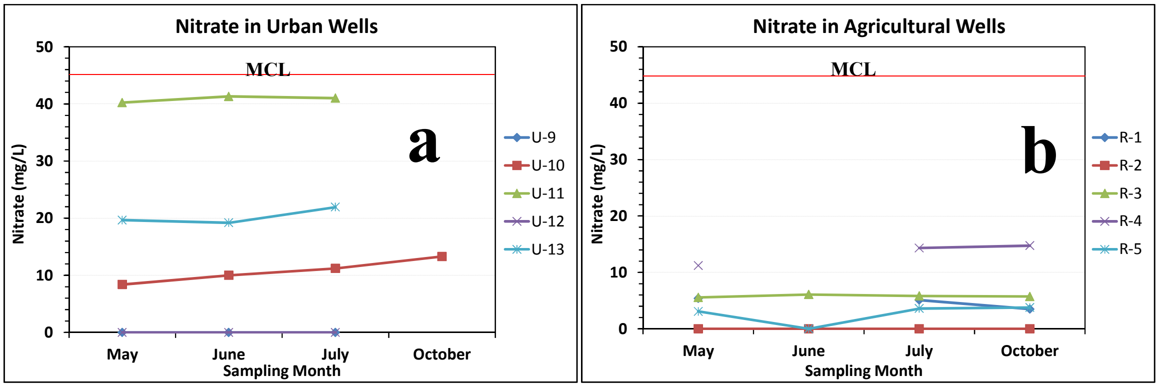


Figure 46. Nitrate in groundwater.

within each site. In urban wells, the highest nitrate concentration was observed in well U-11 and the lowest in well U-12 as well as U-9. Except wells U-9 and U-12, all other wells in urban areas showed high nitrate compared to that in agricultural wells (Figure 46).

Within the agricultural wells, R-4 showed the highest concentration (more than 10 mg/l). Depths of the four agricultural wells (R-1 to R-4) were 195 ft, 205 ft, 70 ft, and 100 ft respectively. Relatively high concentrations in wells R-3 and R-4 can be related to low depth and high nitrate concentration in agricultural soil. Concentrations in all other wells were below 10 mg/l. The reason behind the high nitrate concentration in groundwater wells in urban areas was unclear. It is quite possible that these wells are impacted by deep regional flow of groundwater within the aquifers.

Agricultural soil had the highest nitrate concentration and wetland soil had nitrate below detection level. Urban soils had higher nitrate compared to stream bank soils. Urban sites along the edge of the residential areas and close to the stream channels had low soil nitrate compared to other urban sites. On the other hand, stream bank soils in agricultural land had the highest nitrate and sites along the edge of the urban areas had nitrate below detection level. Stream water from agricultural lands showed higher nitrate values compared to the stream water from urban areas. Wetlands had very low nitrate and prairie water had nitrate below detection.

In the study area, the major flux of nitrate is from the agricultural lands. Urban areas are contributing a portion to that flow of nitrate. Nitrate coming from the agricultural and the urban areas travels to the stream channels through surface runoff and base flow. Wetlands considerably reduce nitrate from the flow system because topographically wetlands are between the urban areas and the drainage ways. Nitrate comes to the stream channels mainly in the months of May and June when there are high agricultural activities.

Vertical distribution of soil nitrate in all hydrologic units indicates effective downward movement of nitrate with water. In groundwater, nitrate concentration was high in urban areas compared to agricultural areas. Temporal variations in groundwater nitrate within each site were unpredictable as the study period was short (May to October). In general, spatial and temporal variations of nitrate concentration in different hydrologic units indicate that nitrate is actively moving through the watershed. Also, different hydrologic units are actively interacting with each other to facilitate this movement.

Total Phosphorus

Surface runoff, generated by storm or rain events, transports nitrogen and phosphorus from agricultural and urban lands to stream channels (Tong and Chen, 2002). Soil erosion can mobilize phosphorus from various sources (Iqbal et al., 2006). This phosphorus may be more erodible earlier in the growing season (Tong and Chen, 2002). Phosphorus is not directly toxic to human health (U.S. EPA 2013 b). EPA does not have a MCL for phosphorus in drinking water but the recommended level for TP (PO_4^{3-}-P) in rivers is less than 100 µg P/l. For lakes and reservoirs the recommended level is 50 µg P/l because concentrations more than this limit can cause eutrophication (U.S. EPA 2013 b).

Total Phosphorus in Agricultural Soil

In agricultural soil, average TP concentration in surface soil (at 0 inch depth) was 149 µg/g (range: 18 to 211 µg/g) in May, 50 µg/g (range: 12 to 108 µg/g) in July and 50 µg/g (range: 11 to 210 µg/g) in October. Average TP at 6 inch depth was 162 µg/g (range: 17 to 422 µg/g) in May, 45 µg/g (range: 12 to 80 µg/g) in July, and 46 µg/g (range: 11 to 110 µg/g) in October. Average TP at 12 inch depth was 78 µg/g (range: 0.1 to 211 µg/g) in May, 51 µg/g (range: 10 to 108 µg/g) in July, and 42 µg/g (range: 3 to 210 µg/g) in October (Figure 47).

The highest TP concentration was observed in May, after which it went down to mostly 200 µg/g or lower (except site R-5 in October) (Figure 47). In fact, after May the TP concentration went down in each depth profile at every site. Most decrease in TP concentration occurred in surface soil profiles (Figure 47). May and June were the peak growing season when P was transported through soil erosion. Low TP after May could be the result of plant uptake early in the season (May to June) and also the surface run off during that time. Similar to nitrate, fluctuations of TP concentration in different depth profiles in successive months were not that prominent. This might be because of phosphorus being less soluble in water compared to nitrate and due to the lack of

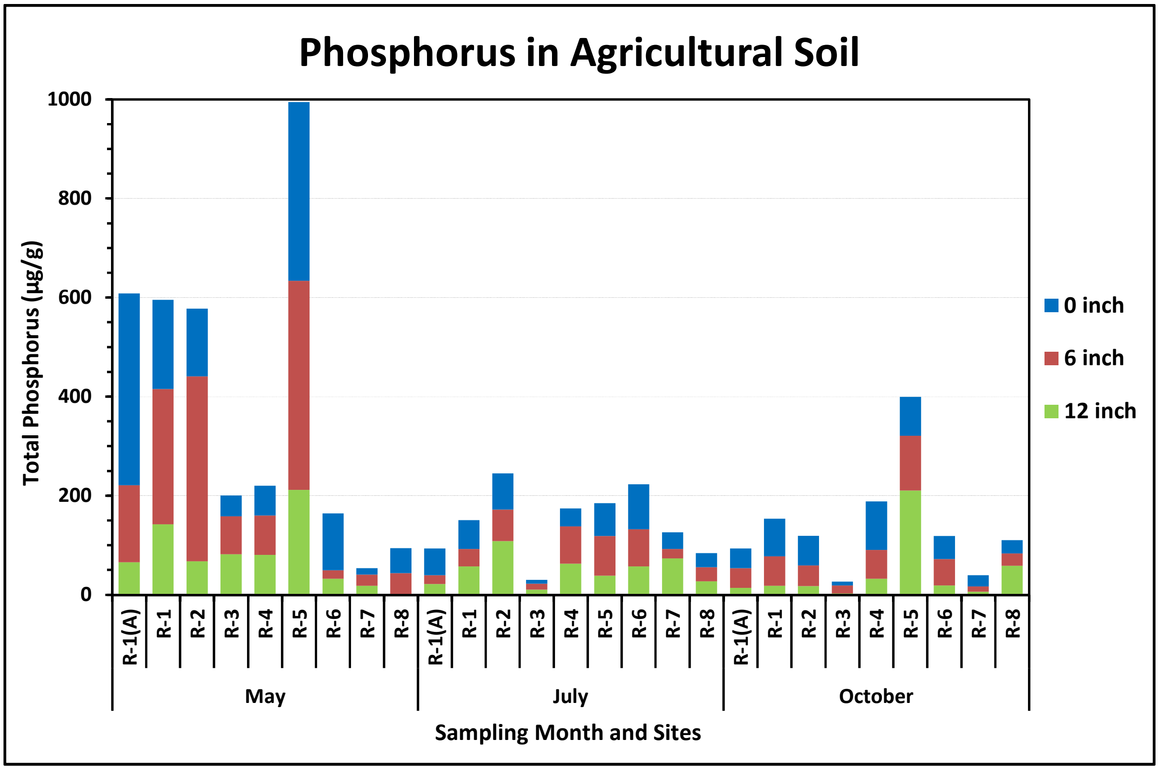


Figure 47. Total phosphorus in agricultural soil.

significant rains during the study period. Thus, the downward vertical movement of TP was limited (Figure 47). The observed spatial variation of TP could be due to the variation of crop pattern, topography, and soil types. Sites with soybean (R-4, R-7, and R-8) showed minimal temporal variation compared to sites in the corn fields (R-1(A) to R-3, and R-5) (Figure 47).

Total Phosphorus in Urban Soil

In urban areas, average TP in surface soil (0 inch depth) was 115 µg/g (range: below detection to 285 µg/g) in May, 40.2 µg/g (range: 14 to 88 µg/g) in July, and 35 µg/g (range: 4 to 80 µg/g) in October. Average TP at 6 inch depth was 87 µg/g (range:

below detection to 278 µg/g) in May, 25 µg/g (range: 2 to 53 µg/g) in July, and 19 µg/g (range: 0.1 to 70 µg/g) in October. Average TP at 12 inch depth was 132 µg/g (range: below detection to 284 µg/g) in May, 30.4 µg/g (range: 5 to 72 µg/g) in July, and 23 µg/g (range: below detection to 210 µg/g) in October (Figure 48).

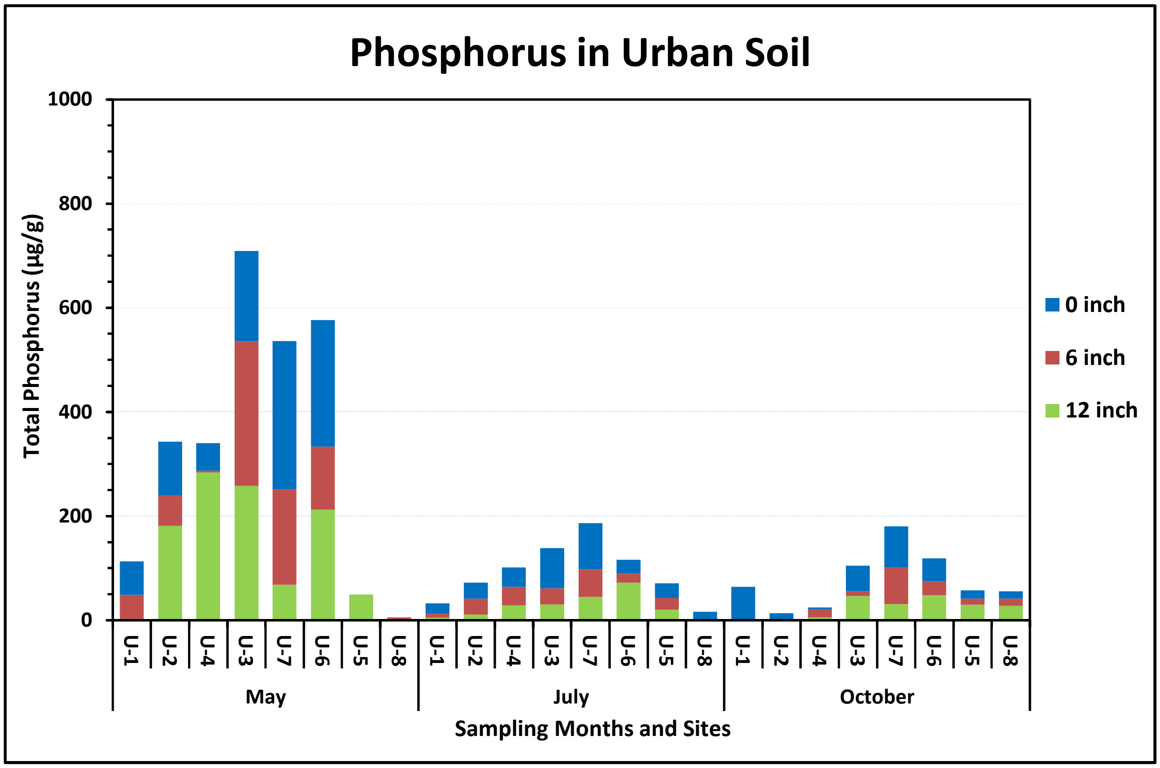


Figure 48. Total phosphorus in urban soil.

The highest TP concentration was observed in May, after which it went down to less than 200 µg/g (Figure 48). After May, TP concentration went down in each depth profile at every site. Most decrease in TP concentration occurred in surface soil profiles (Figure 48). The main source of TP in urban soil was fertilizers used in lawn or golf courses. Low TP after May could be the result of plant uptake over the months of May and June and also surface runoff during that time.

Sites (U-1, U-2, U-4. U-5, and U-8) located along the edge of the urban areas or the upstream areas showed relatively less TP compared to sites (U-3, U-7, and U-4) located in the center of the watershed or further downstream (Figure 16 and 48). This could be due to the flow of suspended sediments through surface runoff converging downstream or to the center of the watershed. By this process, eroded soils carry P from the surrounding areas to the receiving ends. Suspended sediments deposited in downstream areas will then increase P concentration in soil through lateral spreading and deposition.

Fluctuations of TP concentration in different depth profiles in successive months were not that prominent as it was in case of nitrate. This was because phosphorus is less soluble in water compared to nitrate and there was little rain during the study period. Thus, downward movement of TP in the soil was limited (Figure 48).

Total Phosphorus in Stream Bank Soil

In stream bank samples, average TP in surface soil (0 inch depth) was 11.4 µg/g (range: below detection to 30.3 µg/g) in May, 3.8 µg/g (range: below detection to 14.2 µg/g) in July, and 3 µg/g (range: below detection to 12 µg/g) in October. Average TP at 6 inch depth was 12.5 µg/g (range: below detection to 36.7 µg/g) in May, 10 µg/g (range: below detection to 42 µg/g) in July, and 5 µg/g (range: below detection to 14.5 µg/g) in October. Average TP at 12 inch depth was 12 µg/g (range: below detection to 62 µg/g) in

May, 10 µg/g (range: below detection to 43 µg/g) in July, and 6 µg/g (range: below detection to 19 µg/g) in October (Figure 49).

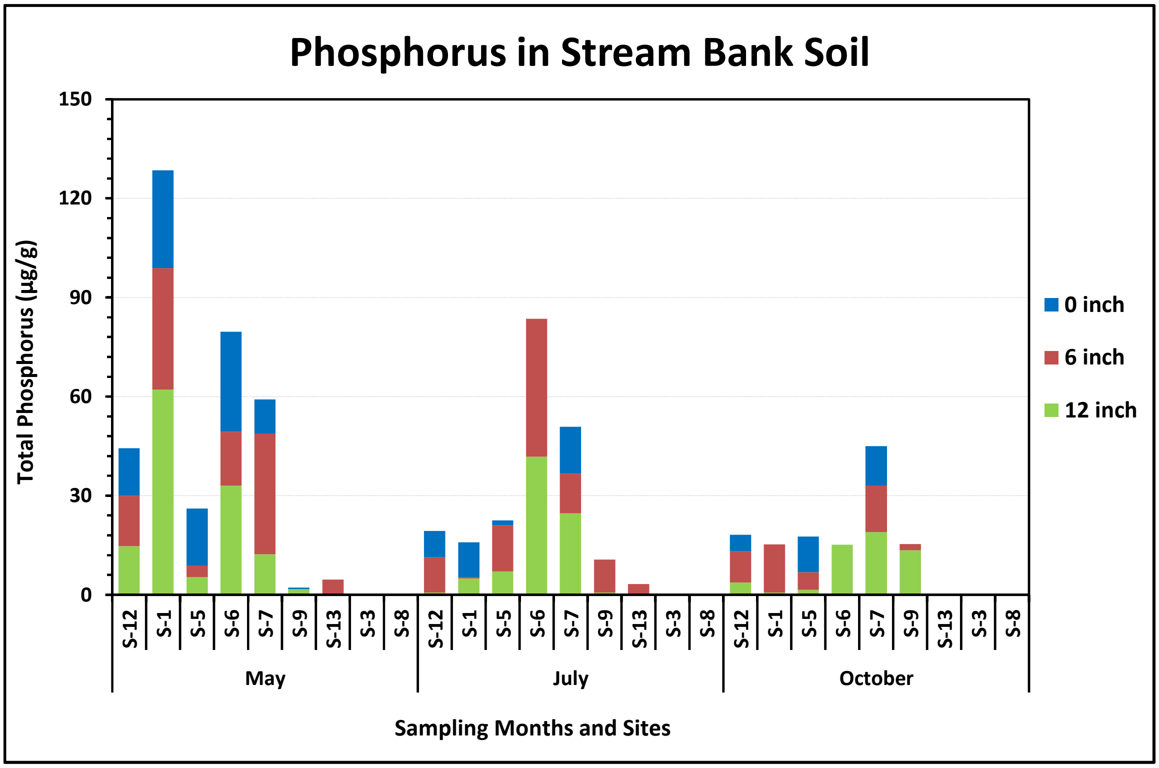


Figure 49. Total phosphorus in stream bank soil.

Relatively high TP was observed in May, after which it went down to below 30 µg/g in most sites (Figure 49). Almost every site showed a sharp decrease of P in surface soil after May. This may be due to the loss of soil by surface runoff over the early part of the season. Sites located in agricultural areas (S-12) and those that received flows from both agricultural and urban areas (S-1, S-5 to S-7) showed relatively high P concentrations. On the other hand, sites in downstream areas (S-8) or the areas that received water from urban areas only (S-3) showed P concentration below detection level (Figure 49).

Total Phosphorus in Wetland Soil

In wetland soil, average TP in surface soil (0 inch depth) was 105 µg/g (range: 1 to 250 µg/g) in May, 28 µg/g (range: 1 to 127 µg/g) in July, and 2.3 µg/g (range: below detection to 5 µg/g) in October. Average TP at 6 inch depth was 82 µg/g (range: 6.4 to 180 µg/g) in May, 26 µg/g (range: 2 to 95 µg/g) in July, and 2.6 µg/g (range: below detection to 8.6 µg/g) in October. Average TP at 12 inch depth was 44 µg/g (range: 18 to 90 µg/g) in May, 13 µg/g (range: 3 to 23 µg/g) in July, and 3 µg/g (range: below detection to 10 µg/g) in October (Figure 50).

Relatively high TP was observed in May, after which P concentration went down to below 50 µg/g in most sites (Figure 50). This wetland also served as a flood water retention basin and it is connected to several other retention ponds upstream. During floods, this system stores additional water that is slowly released through an outlet (Figure 16). Flood water usually stays in this basin for a few days and deposits suspended sediments that are carried by runoff water from the surrounding areas. High levels of P adsorbed to these sediments seem to be the reason why the inlet points (W-3 and W-4) have P concentrations that are so high in May (Figure 50). As P takes time to liberate from binding particles and start moving into the system after May, P concentration in soil gradually goes down.

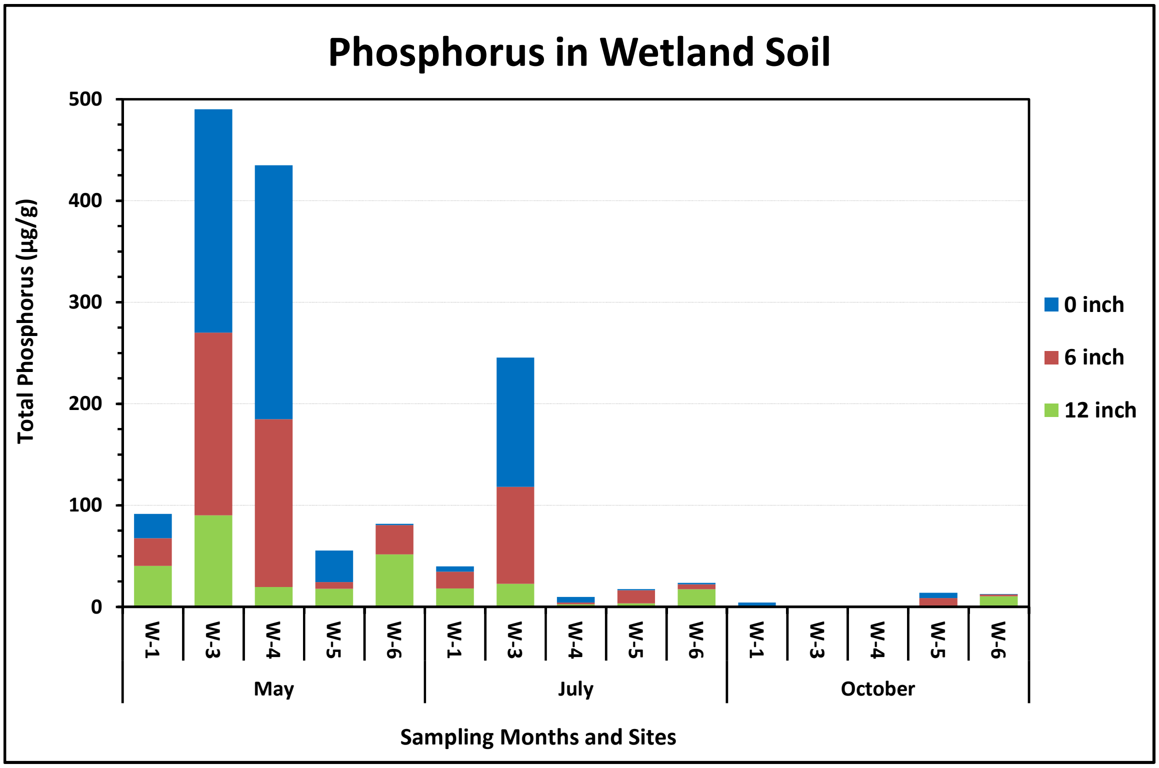


Figure 50. Total phosphorus in wetland soil.

Total Phosphorus in Prairie Soil

In prairie soil, average TP in surface soil (0 inch depth) was 123 µg/g (range: 72 to 161 µg/g) in May, and 74 µg/g (range: 53 to 99 µg/g) in October. Average TP at 6 inch depth was 202 µg/g (range: 153 to 366 µg/g) in May, and 136 µg/g (range: 65 to 249 µg/g) in October. Average TP at 12 inch depth was 247 µg/g (range: 153 to 367 µg/g) in May, and 127 µg/g (range: 76 to 190 µg/g) in October (Figure 51).

Increased acidity in soil due to plant root respiration can release significant amounts of adsorbed P from soil. In addition, soil rich in the mineral apatite can have higher content of P. Although the exact percentage of apatite in area soils is unknown, the

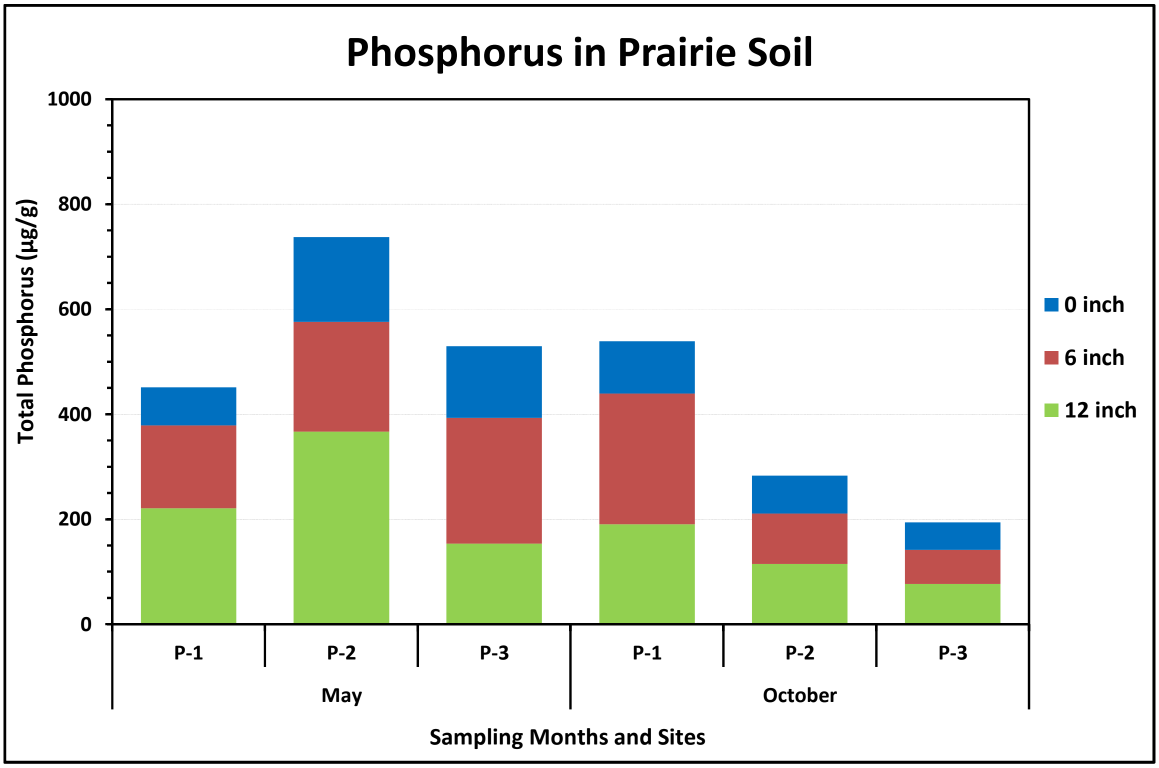


Figure 51. Total phosphorus in prairie soil.

relative high level of P in Cedar Hills Sand Prairie is attributed to a combination of the above two reasons. Besides, the prairie soil is pristine (free from any anthropogenic activities and no external source of nutrient) and the observed P in this soil must be the result of long term accumulation of P from decayed vegetation. Overgrowth of plants can create an anoxic condition through their decay, causing P to be fully released from soil.

Total Phosphorus in Surface Water

In stream water, average TP was 42 µg/l (range: 19 to 120 µg/l) in May, 69 µg/l (range: 22 to 174 µg/l) in July, 1.5 µg/l (range: below detection to 18 µg/l) in August, and 161 µg/l (range: 64 to 483 µg/l) in October (Figure 52).

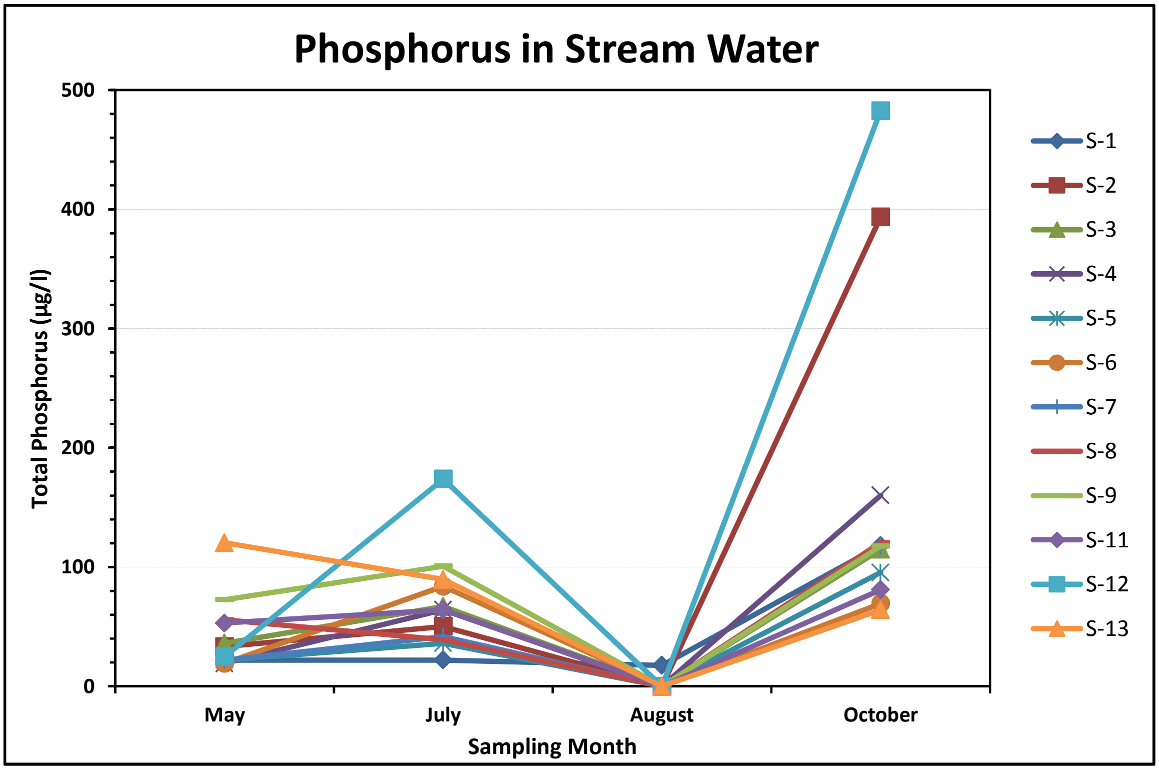


Figure 52. Total phosphorus in stream water.

TP in most of the sites was below the EPA recommended level of 100 µg P/l (Figure 52). Phosphorus concentration was relatively low in May. The average concentration went up in July slightly, and then dropped to almost nothing in August and finally it increased considerably in October. In August, only one site (S-1) had detectable TP value, with all other sites below detection level. Unlike nitrogen, P is slow moving in the system and during the study period there were only a few rain events (Figure 14-15). These could be the reason why TP values increased only after August. During July and August agricultural lands were covered by crops so the release of soil runoff P was not significant. By the end of August, crops had been harvested and the agricultural fields became more open to soil loss all the way to October. In addition, fields had accumulated enough plant residues by then to cycle P from decayed vegetation to the soil. The accumulated P is also expected to impact the waterways in the fall. Phosphorus coming from the urban areas was mainly because of the fertilizers used in lawns, athletic fields and golf courses. Except sites S-12 and S-2 in October, average TP concentration was within the range of what was reported by Shrestha (2008) and IOWATER (2010).

Figure 53 shows the TP concentration in different sub-watersheds of DRC and the Cedar River (Figure 20 and 21). In sub-watershed-6 (Figure 53 a), the main source of P is both urban and agricultural areas as there was not much variation in TP values among these sites. In sub-watershed-7 (Figure 53 b), the main source of P is site S-12, which is located in agricultural areas (Figure 16).

In sub-watershed-1 (Figure 53 c), P was mainly coming from S-3, which is located in an urban area. In sub-watersheds-6 and 7, TP in water was relatively low when the main channels of those sub-watersheds entered into the urban areas (Figure 16 and 53). This might be the effect of dilution as these channels received surface runoff from urban areas that had low TP compared to the agricultural areas. Due to this dilution, even though the P concentrations in upstream areas of these sub-watersheds were high, they became lower when they all entered the Cedar River through site S-8 (Figure 20 and 53). As a result, though upstream sites of DRC had higher P concentrations compared to the Cedar River, P concentration appeared higher in the Cedar River compared to DRC at site S-8 (Figure 53 d).

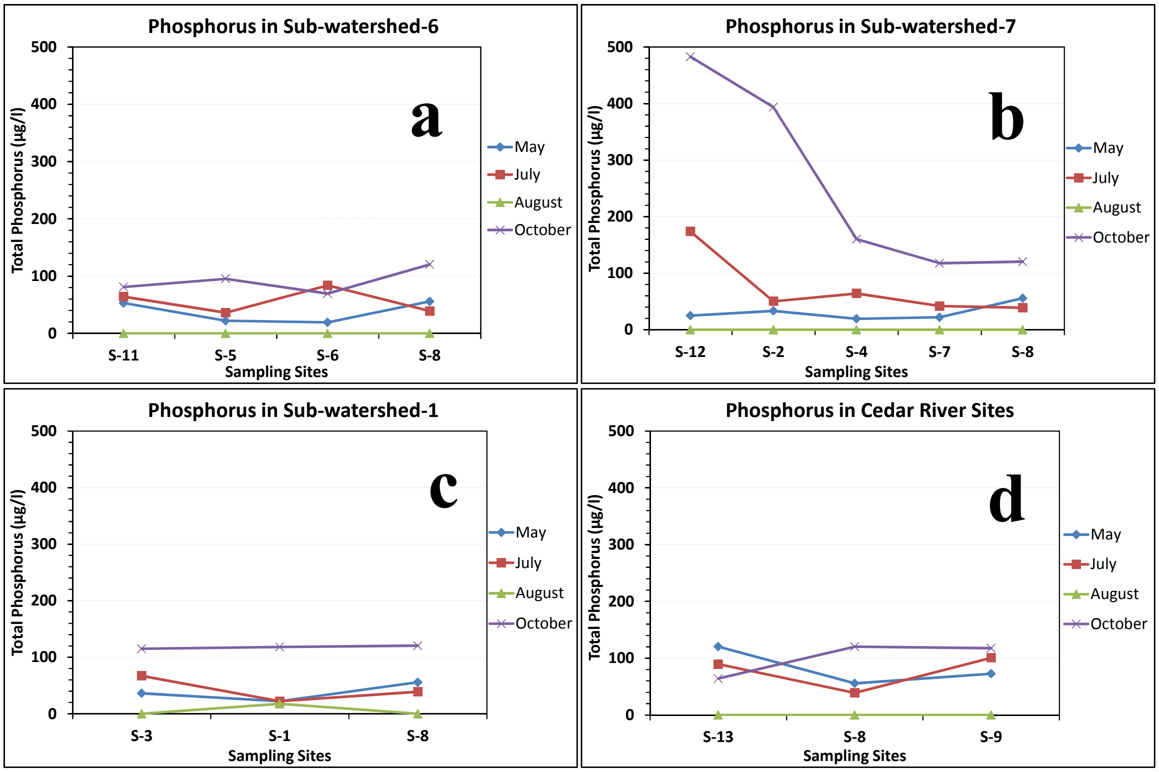


Figure 53. Total phosphorus in different sub-watersheds of DRC and Cedar River.

In wetland water, average TP was 45 µg/l (range: 22 to 88 µg/l) in May, 56 µg/l (range: 25 to 114 µg/l) in July, 47 µg/l (range: 22 to 99 µg/l) in August, and 28 µg/l (range: 20 to 38 µg/l) in October (Figure 54). The site W-3, which received water from the surrounding urban areas, had the highest P value compared to the other sites. Almost every site had TP values less than the EPA recommended 100 µg/l of P for surface water bodies.

In prairie water, average TP was 174 µg/l (range: 48 to 390 µg/l) in May and 59 µg/l (range: 55 to 67 µg/l) in October (Figure 55). Sometimes standing water bodies in prairies can have unexpectedly high dissolved P. This occurs due to the anoxic conditions

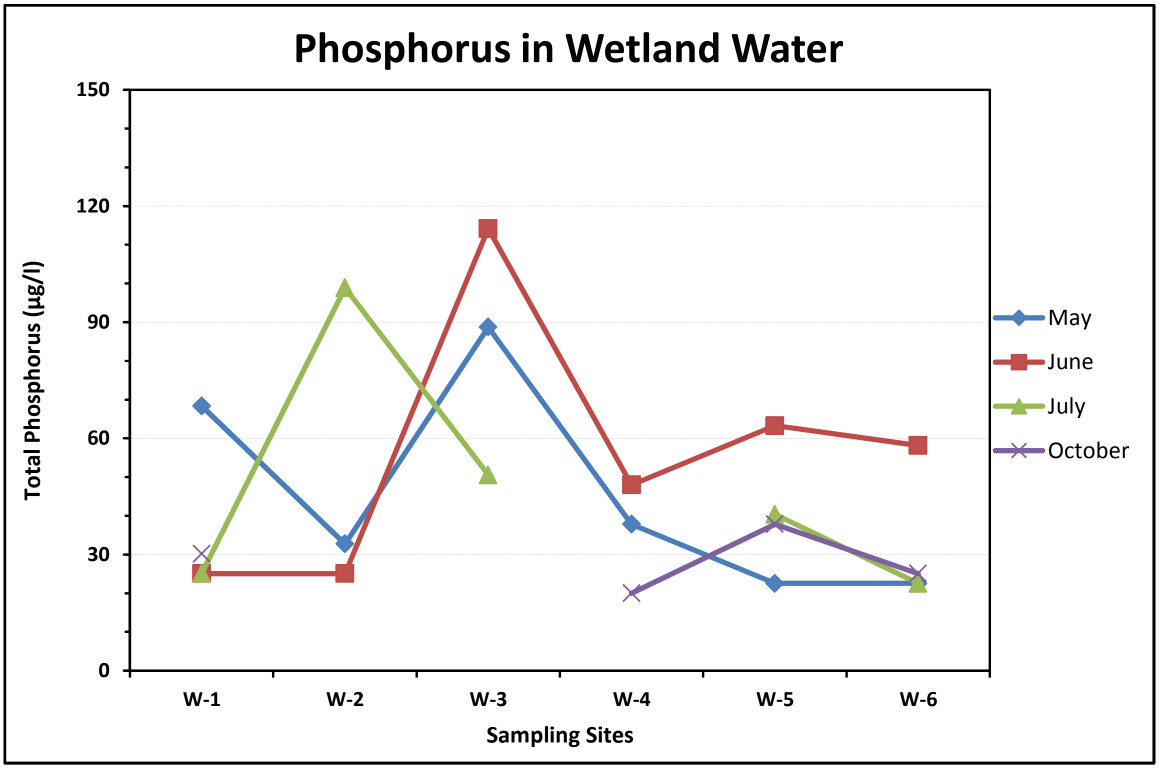


Figure 54. Total phosphorus in wetland water.

created by the decay of overgrown aquatic plants. In low oxygen conditions, the soil particles to which P remains attached are dissolved. As a result, the P becomes available in the water column.

Total Phosphorus in Groundwater

In urban wells, average TP was 3 mg/l (range: 14 to 25 mg/l) in May, 6 mg/l (range: 14 to 30 mg/l) in June, and 9 mg/l (range: below detection to 28 mg/l) in July (Figure 56 a). In agricultural wells, average TP was 5 mg/l (range: 25 to 43 mg/l) in May, 3 mg/l (range: 16 to 25 mg/l) in June, 8 mg/l (range: 16 to 46 mg/l) in July, and 5 mg/l (range: 16 to 31 mg/l) in October (Figure 56 b).

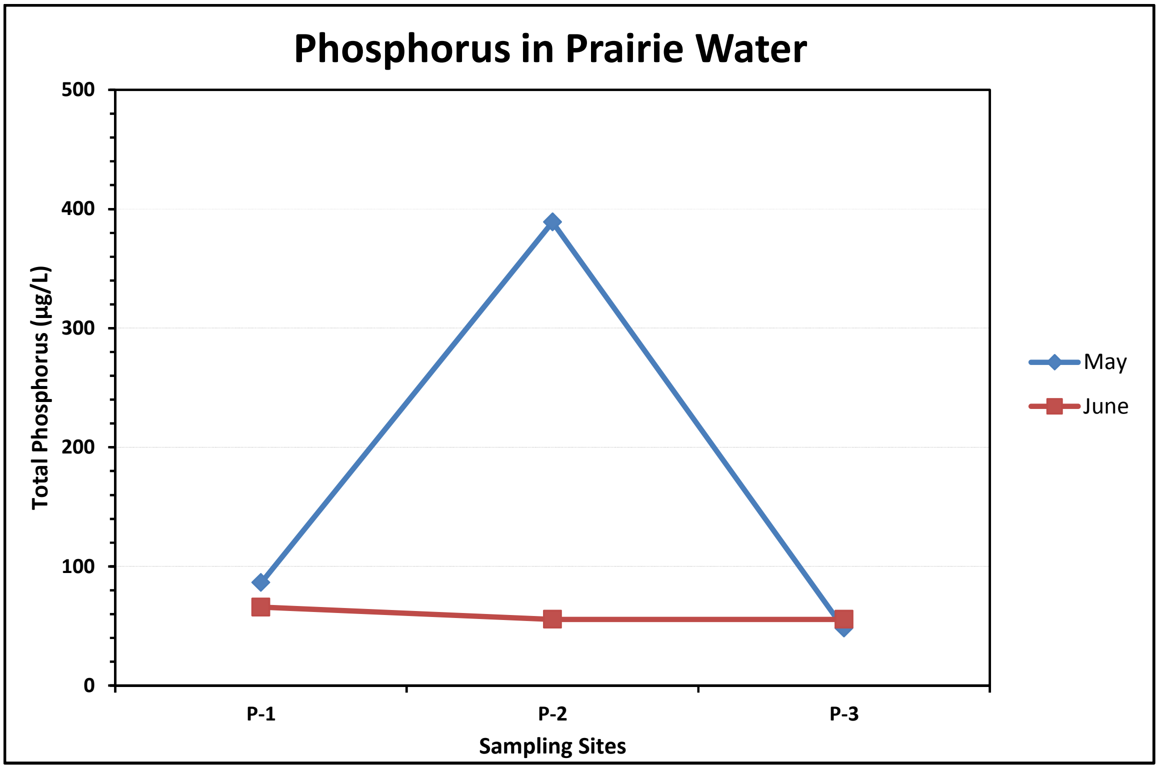


Figure 55. Total phosphorus in prairie water.

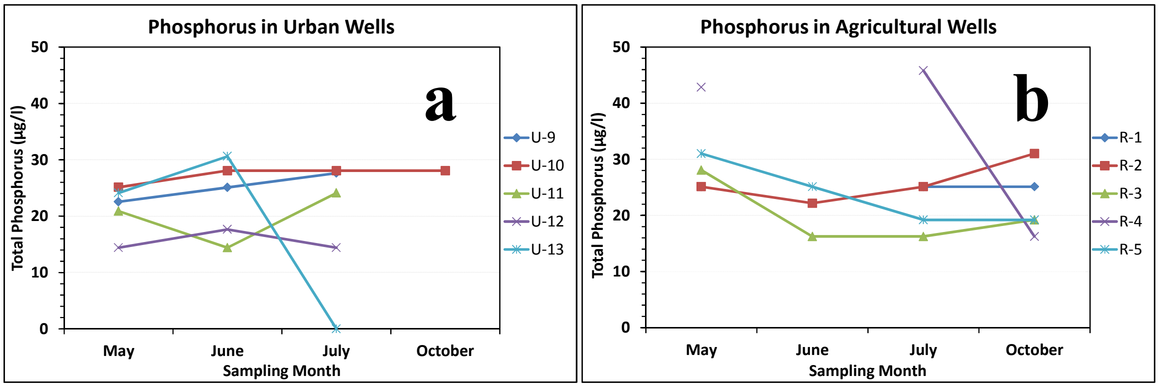


Figure 56. Total phosphorus in groundwater.

There was no difference between the urban wells and the agricultural wells in terms of TP concentration (Figure 56). Urban wells showed slightly increasing trend from

May to October. On the other hand, agricultural wells showed slightly decreasing trend during the same time period (Figure 56).

In general agricultural soils had the highest TP values followed by prairie, urban, wetland and stream bank soils (Figure 47-51). In all hydrologic units, there was a sharp decrease in soil TP concentration after May. This can be correlated with the agricultural activities and the rain fall pattern in the area. There were no spatial variations in TP within the agricultural soils. In urban soil, TP values showed a gradual increase toward the central portion of the urban areas.

Both agricultural and urban areas had high and low TP values throughout the study period. Thus, both of these areas seem to have delivered P to the stream channels. Vertical movement of P was not clear as there were low amounts of rainfall during the study period and P is less soluble in water compared to nitrate. Wetland sediments had high TP values, probably due to the accumulation of suspended sediments during flood events. Sub-watershed-7 seems to have delivered more P compared to the other sub-watersheds in the DRC watershed (Figure 53). No significant variations in TP values were found in groundwater.

Chloride

Chloride ions are very common in all natural waters. In small amounts they are not significant. But in large concentrations they present problems. In nature, major forms of chloride are sodium (NaCl) and potassium (KCl) salts (Mashburn and Sughru, 2003). Potassium chloride is used in the production of fertilizers. Chloride also indicates human or animal waste contamination in the stream (Mashburn and Sughru, 2003).

Anthropogenic sources of chloride include septic waste, wastewater effluent, industrial waste, animal waste, fertilizer, de-icing salts, and produced water from oilfield operations (Mashburn and Sughru, 2003). The EPA Secondary Drinking Water Regulations recommend a maximum concentration of 250 mg/L for chloride ions (U.S. EPA, 2013 b). In this study, soil chloride concentration was measured using the same methods as in nitrate.

Chloride in Agricultural Soil

Out of the nine sites sampled in agricultural soil, three sites in May, four sites in June, six sites in July, and five sites in October had chloride concentrations below the detection level (Figure 57). In most of the sites, total chloride concentrations in all depth profiles were below 100 mg/kg.

Chloride concentrations in most upstream sites went down (R-1A and R-2 to R-5) after May. On the other hand, some downstream sites (R-6 and R-7) showed measurable chloride after May even though no chloride was detected earlier (Figure 16 and 57). Again in October, chloride showed up in upstream sites but not in sites that were downstream. This was an indication of chloride movement from upstream to the downstream areas of the watershed. De-icing salt from winter and manure from agricultural fields might have contributed chloride in May. Chemical fertilizers used in the fields during the summer months are the primary sources of chloride in late summer and fall. Chloride is very soluble in water. It moves with water easily, thereby causing the agricultural soil to have ups and downs in chloride concentrations both spatially and vertically in different depth profiles (Figure 57).

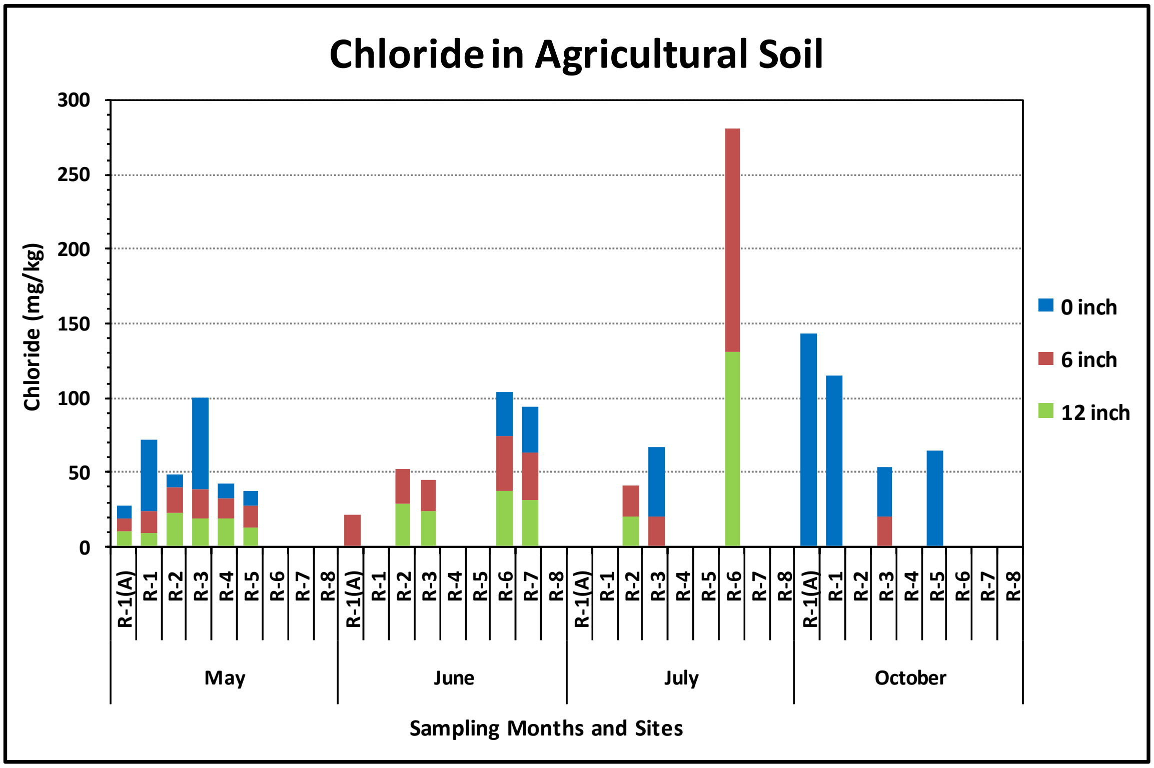


Figure 57. Chloride in agricultural soil.

Chloride in Urban Soil

Out of eight sites in urban soil, three sites in May, six sites in June, two sites in July, and three sites in October had chloride concentrations below the detection level (Figure 58). In most of the sites total chloride concentrations in all depth profiles were below 100 mg/kg. The lowest chloride concentration was found in July. After July, almost all sites experienced an increase in chloride concentration. Relatively high chloride in July and October is attributed to the lawn fertilizers applied in residential areas. High solubility of chloride in water made frequent ups and downs in chloride

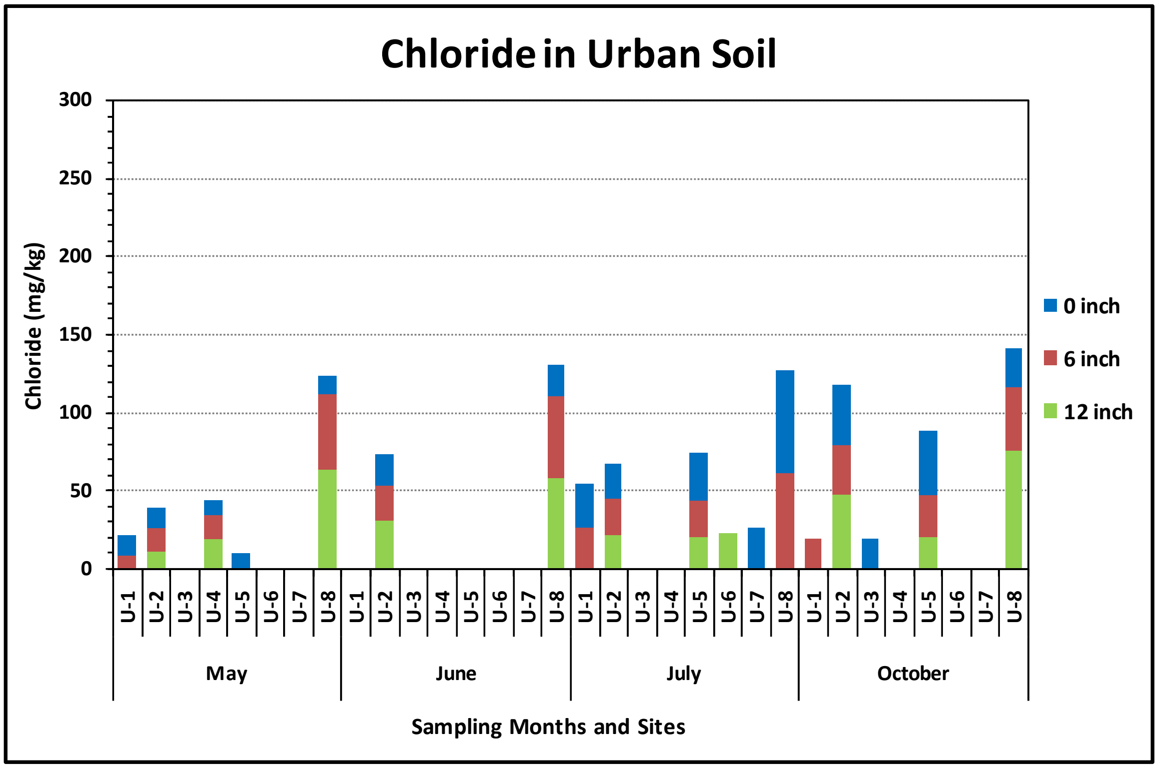


Figure 58. Chloride in urban soils.

concentrations both spatially and temporally. Solubility seems to have made an impact on vertical distribution of chloride as well.

Chloride in Stream Bank Soil

Out of nine sites in stream bank soil, eight sites in May, four sites in June, three sites in July, and six sites in October had chloride concentrations below detection level (Figure 59). Though many sites had chloride below the detection level, some sites showed high concentrations. Almost 50% of the sites that detected chloride showed concentration levels more than 200 mg/kg. The lowest chloride concentration was in May. Most stream bank chloride was observed during the months of June and July,

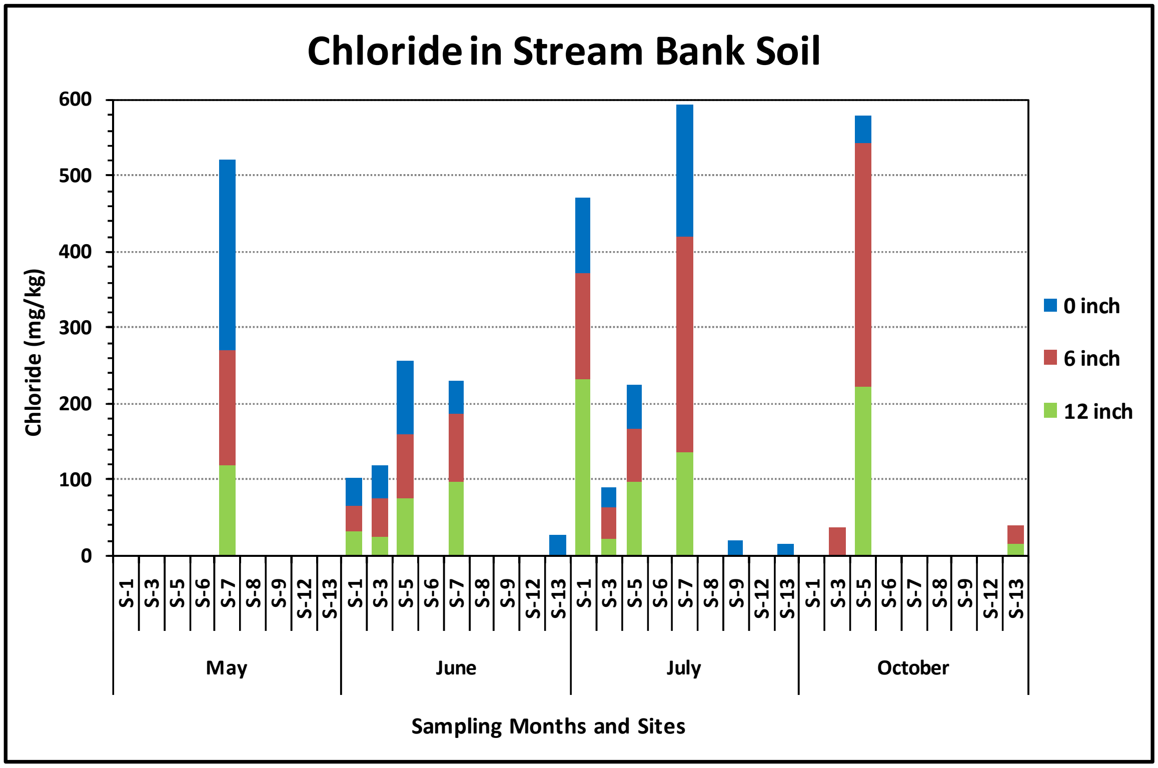


Figure 59. Chloride in stream bank soil.

indicating this effective transport from the upland area to the drainage ways. Stream bank soil frequently showed high chloride in sites around urban areas (S-1 to S-3, and S-7) (Figure 16 and 59). This indicates long term impact of city sewerage systems as well as industrial waste stream from urban areas.

Chloride in Wetland Soil

Out of five sites in wetland soil, three sites in May, two sites in June, one site in July, and three sites in October had chloride concentrations below the detection level (Figure 60). Almost 50% of the sites that had detectable chloride showed concentration levels more than 100 mg/kg. Consistent high chloride was observed in sites located along

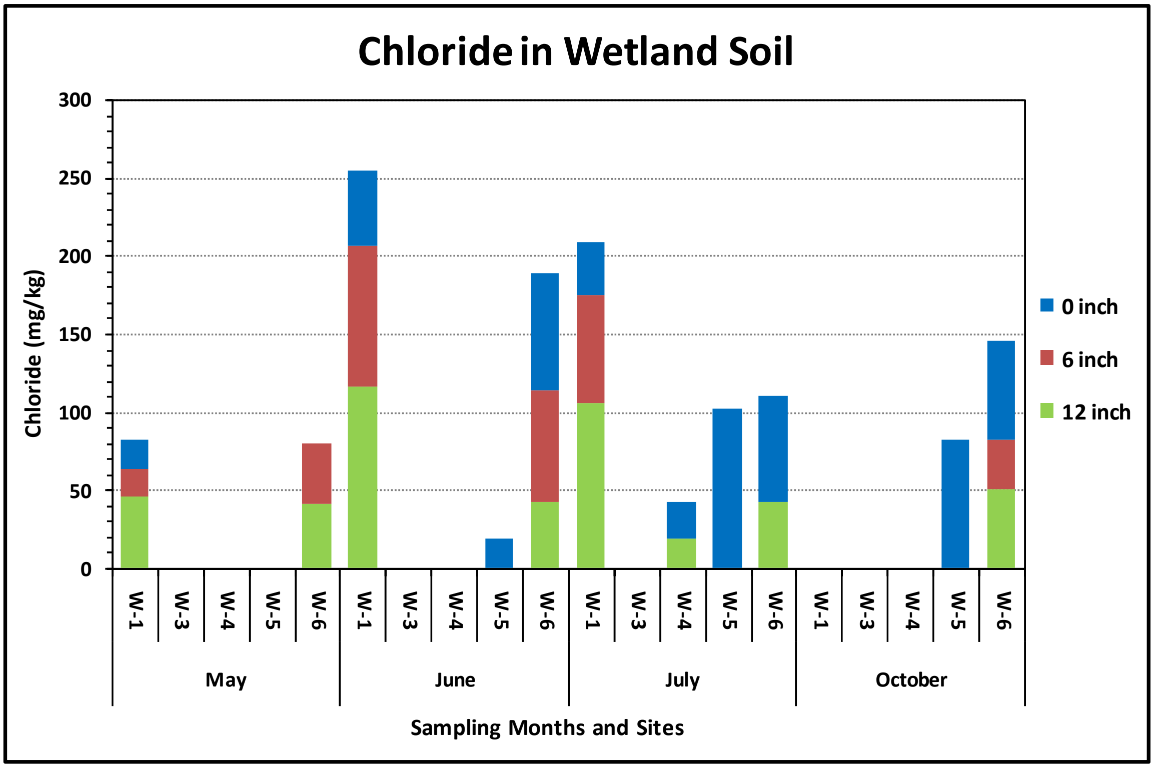


Figure 60. Chloride in wetland soil.

the eastern part of the wetland (W-1 and W-6) (Figure 16 and 60).The eastern part of the wetland is close to urban areas and these sites seem to have received chloride through surface runoff.

Chloride in Prairie Soil

In the prairie, chloride was observed in all sites during the month of June only. In May and October, chloride was below detection level in all samples except at 6 inch depth in P-3. The June concentration of chloride was around 100 mg/kg in all sites (Figure 61).

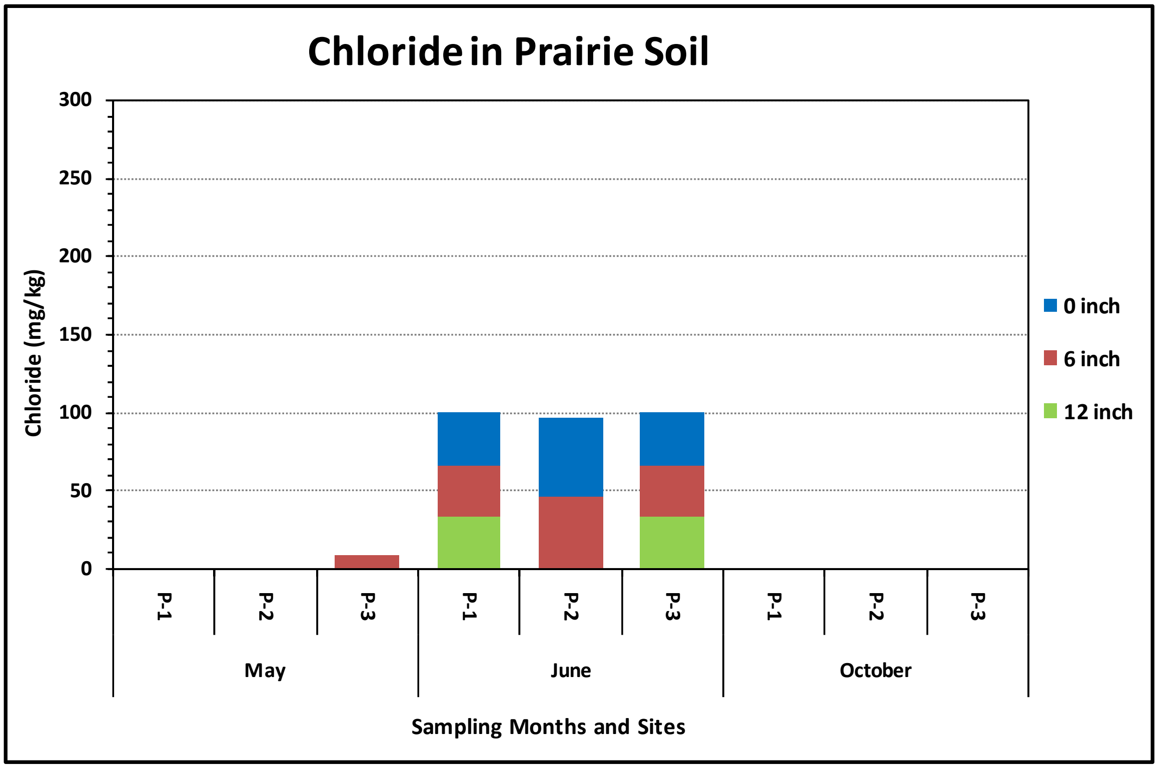


Figure 61. Chloride in prairie soil.

Chloride in Surface Water

In stream water, average chloride concentration was 35 mg/l (range: 11 to 64 mg/l) in May, 31 mg/l (range: 15 to 64 mg/l) in June, 40 mg/l (range: 7 to 118 mg/l) in July, 17 mg/l (range: 12 to 21 mg/l) in August, and 18 mg/l (range: 6 to 54 mg/l) in October (Figure 62).

With the exception of site S-3 chloride concentration in stream water was fairly consistent in May and June; it was the highest in July and much lower in August and October (Figure 62). Higher concentrations were observed at sites S-5, S-6, and S-11. Site S-11 was located near an agricultural area and sites S-5 and S-6 were in urban areas.

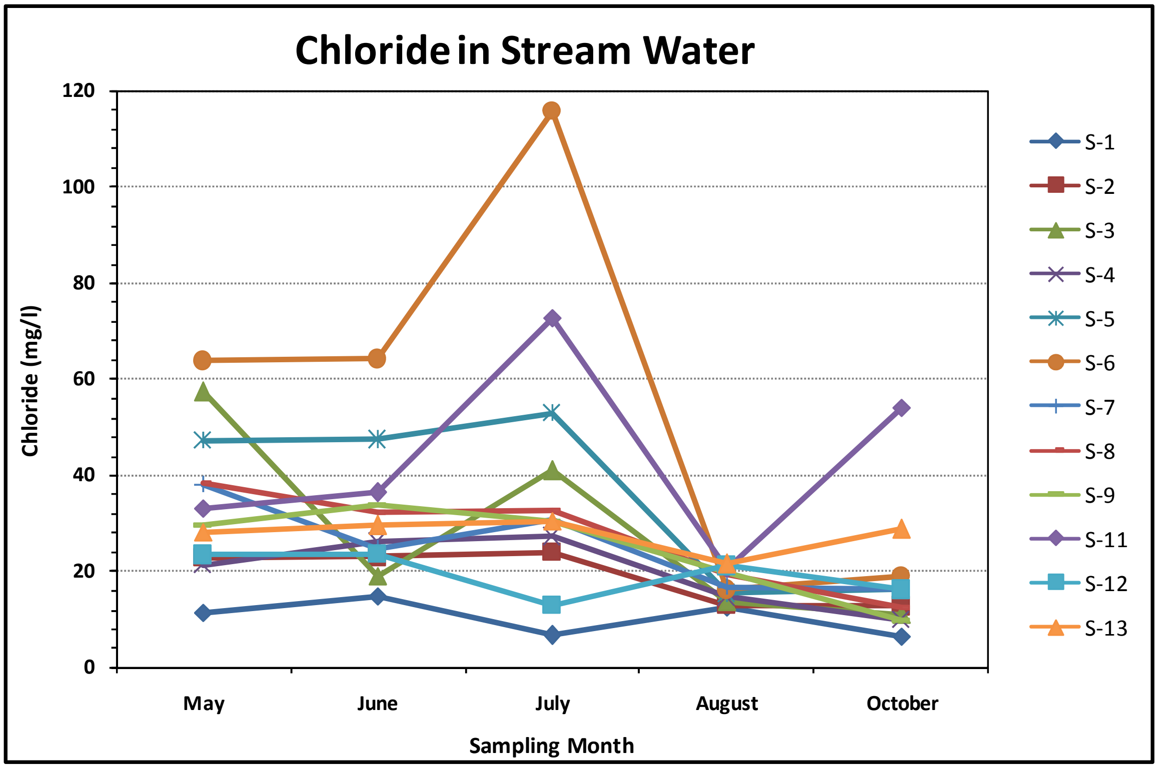


Figure 62. Chloride in stream water.

Surface water chloride concentration was within the range of what was reported by Shrestha (2008) and IOWATER (2010).

In wetland water, average chloride concentration was 34 mg/l (range: 4 to 66 mg/l) in May, 32 mg/l (range: 3 to 58 mg/l) in June, 21 mg/l (range: 4 to 46 mg/l) in July, and 55 mg/l (range: 31 to 103 mg/l) in October (Figure 63). In wetland water, chloride concentrations were generally consistent in all sites except in October (Figure 63). The inlet points and the central water body (W-2 to W-4 and W-5) had higher concentrations compared to the outlet point (W-6) (Figure 16 and 63).

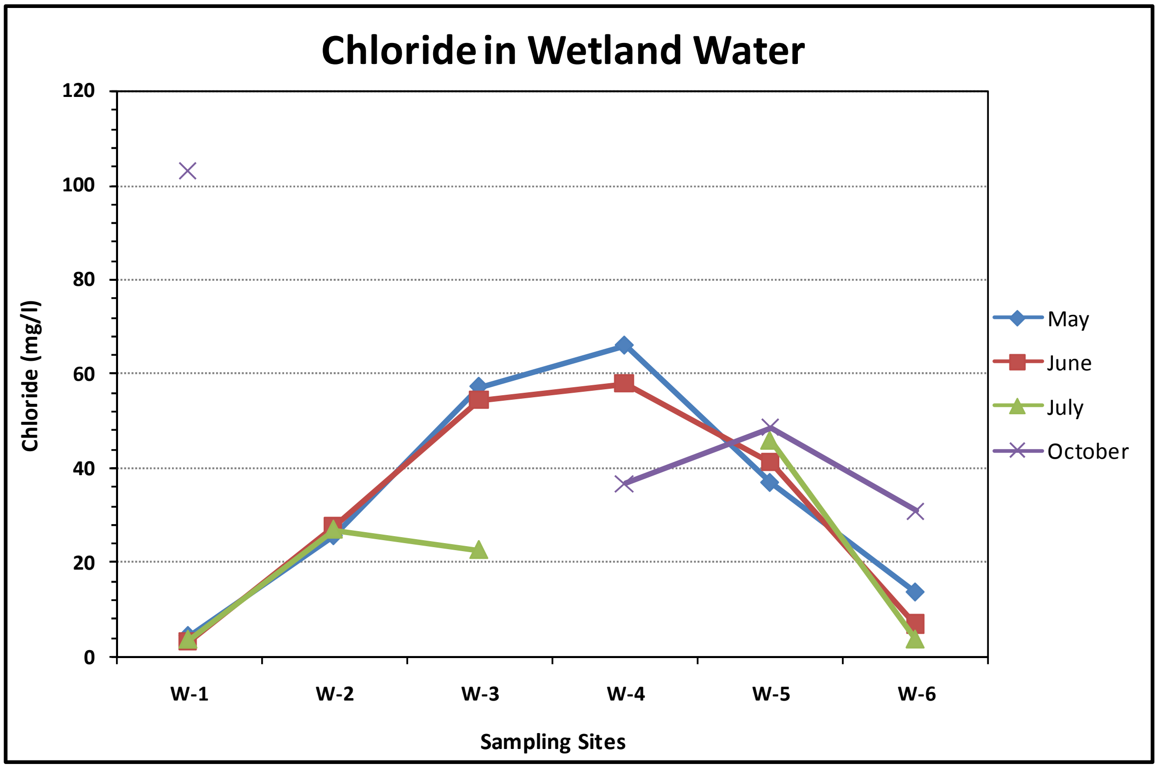


Figure 63. Chloride in wetland water.

Chloride in Groundwater

In urban wells, average chloride concentration was 32 mg/l (range: 9 to 58 mg/l) in May, 35 mg/l (range: 10 to 71 mg/l) in June, and 36 mg/l (range: 10 to 78 mg/l) in July (Figure 64 a). In agricultural wells, average nitrate concentration was 4 mg/l (range: below detection to 11 mg/l) in May, 3 mg/l (range: below detection to 10 mg/l) in June, 4 mg/l (range: below detection to 8 mg/l) in July, and 5 mg/l (range: below detection to 10 mg/l) in October (Figure 64 b). Groundwater samples did not show any temporal variations. There were some spatial variations, probably due to the variations in aquifer

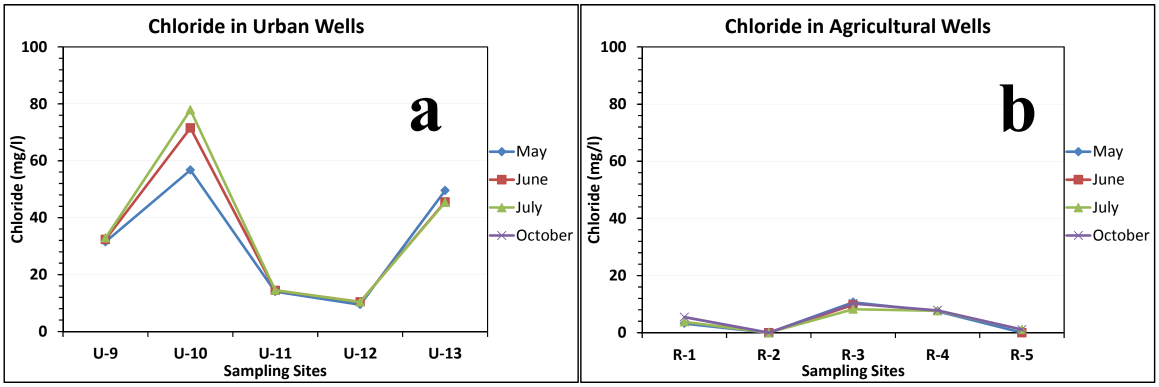


Figure 64. Chloride in groundwater.

materials. In general, agricultural wells had much less chloride compared to the urban wells (Figure 64).

Chloride is very soluble and mobile in water. This must be the reason it didn't show up in every site across hydrologic units. Because of its high solubility, chloride might have been diluted very quickly and didn't show up in every sample. Its mobility in the aquatic system caused its concentration to be high in stream bank soils compared to the other hydrologic units. From the soil and the surface water concentrations it can be said that chloride is derived from agricultural as well as urban areas. Groundwater chloride concentrations didn't vary temporally and agricultural wells had much less chloride compared to urban wells. None of the water wells exceeded EPA recommended MCL for chloride of 250 mg/l.

Sulfate

Sulfate can be found in air, soil and water. Sulfur released to the atmosphere due to fossil fuel combustion is oxidized to sulfate. Through precipitation or by dry deposition sulfate can return to water bodies. Solubility in water made sulfate available at high concentrations in many aquifers and in surface water bodies. Dissolved ionic phase of sulfate makes it mobile in ground water (MPCA, 1999). The EPA Secondary Drinking Water Regulations recommend a maximum concentration of 250 mg/L for sulfate ions (U.S. EPA, 2013 b). Soil sulfate concentration was measured in the same way as described for nitrate. During the study period, sulfate was observed in a few sites of all hydrologic units. In agricultural and urban areas sulfate was mainly observed in May.

In stream water, average sulfate concentration was 20 mg/l (range: 13 to 25 mg/l) in May, 19 mg/l (range: 14 to 28 mg/l) in June, 26 mg/l (range: 9 to 42 mg/l) in July, 17 mg/l (range: 13 to 20 mg/l) in August, and 18 mg/l (range: 8 to 50 mg/l) in October. Sulfate concentrations in stream water were consistent in May and June; it was the highest in July and lower in August and October.

In urban wells, average sulfate concentration was 26 mg/l (range: 13 to 41 mg/l) in May, 26 mg/l (range: 10 to 45 mg/l) in June, and 25 mg/l (range: below detection to 44 mg/l) in July. In agricultural wells, average sulfate concentration was 18 mg/l (range: 14 to 22 mg/l) in May, 24 mg/l (range: 20 to 32 mg/l) in June, 18 mg/l (range: 14 to 22 mg/l) in July, and 20 mg/l (range: 14 to 23 mg/l) in October. Groundwater samples did not show any temporal variations. There were some spatial variations due to the variations in aquifer materials. In general agricultural wells had less sulfate compared to the urban wells.

Total Suspended Sediment

Figure 65 shows the variations in TSS in the DRC watershed. Usually, clear water has TSS less than 20 mg/L and cloudy water has TSS between 40 to 80 mg/L. If the TSS concentration exceed 150 mg/l it considered dirty (Enciso, 2012). In the study area, TSS values are below 20 mg/L (except a few sites in May and one site in August). Most of the sites had low TSS in May, which went up slightly in June. After June, it went down very gradually in all sites and became close to zero in October. One of the two sites in the Cedar River (S-13) showed considerably higher loads after July as expected from a large watershed like this. The other site in the Cedar River (S-9) however has considerably lower TSS. This is attributed to the small dams constructed past S-13 to reduce flow as flood control measures. These measures cause rapid deposition of sediments before they reach S-9.

Load Calculation

Nutrient (nitrate and phosphorus) and TSS loads were estimated for the months of May, July and August. As mentioned earlier, this will give only a general idea about how much nutrient and suspended sediments were derived from different sections of the DRC watershed. Three main sub-watersheds were chosen for this calculation, namely sub-watershed-1, sub-watershed-6, and sub-watershed-7 (Figure 21).

Average nitrate transported in three months (May, July, and August) was 3,582 kg from sub-watershed-1, 62,822 kg from subwatershed-6, and 15,234 kg from sub-watershed-7. Total nitrate leaving the DRC watershed in three months was 244,912 kg (Table 2). Sub-watershed-6 contributed about 77% of nitrate that passed through the

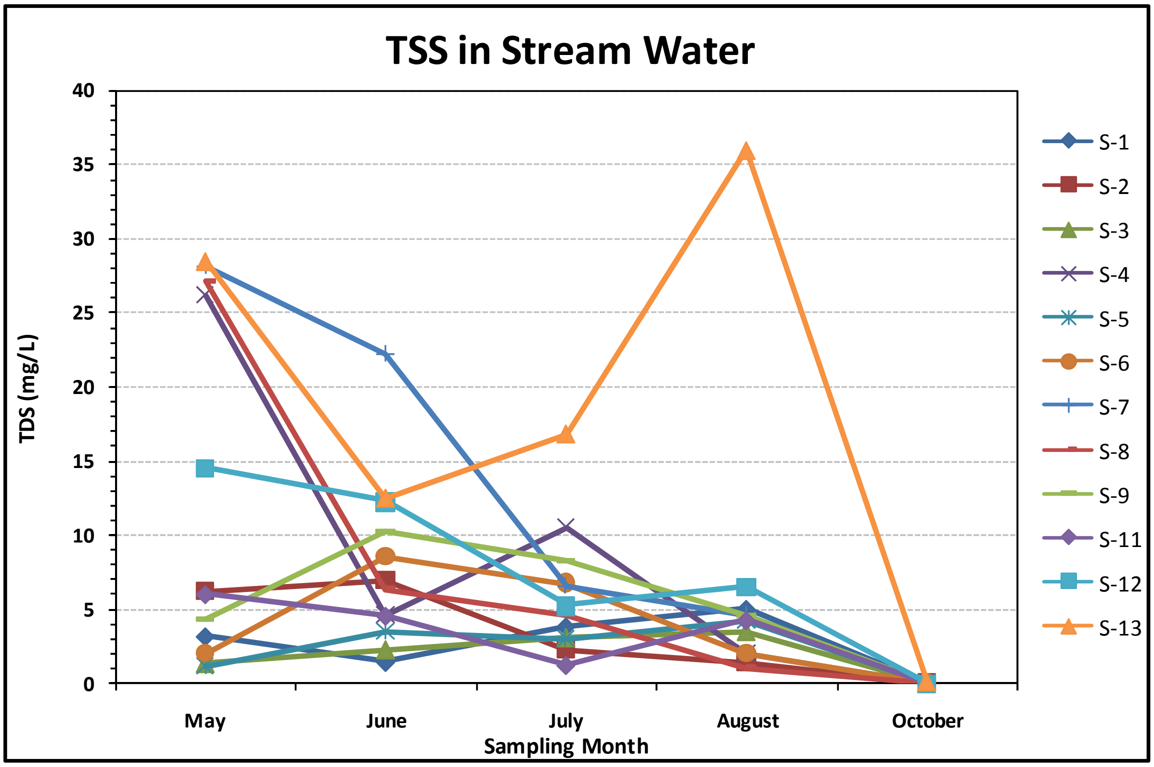


Figure 65. Total suspended sediments in DRC watershed.

Table 2. Nitrate load in DRC watershed.

Nitrate load in Kg				
	May	July	August	Total Nitrate from each watershed
Sub-watershed-1	2,190	1,603	6,952	10,745
Sub-watershed-6	169,748	3,600	15,116	188,465
Sub-watershed-7	37,245	2,134	6,324	45,703
Total nitrate from each month	209,184	7,337	28,391	
			Total nitrate from DRC in three months	244,912

DRC watershed. Most of the nitrate (about 85%) moved through the system in May. This is because of the application of fertilizers and manure in late spring before the next cropping season.

Average P leaving in three months (May, July, and August) was 20 kg from sub-watershed-1, 81 kg from subwatershed-6, and 18 kg from sub-watershed-7. Total P leaving from the DRC watershed in three months was about 594 kg (Table 3). Sub-watershed-6 contributed the major portion (about 41 %) of P that passed through the DRC watershed. Compared to other months, highest amount of P moved through the system in July. This is because phosphorus takes a longer time to get into the hydrologic system compared to nitrate as P is less soluble in water. Total phosphorus load leaving from the DRC was more than the combined load of the three sub-watersheds. This excess phosphorus was coming from the areas of the watershed that were not included in the sub-watersheds (Figure 20 and 21). These areas are mostly downstream urban areas and contributed phosphorus through surface runoff as surface runoff from impervious urban areas contains phosphorus (Tong and Chen, 2002).

Average TSS leaving in three months (May, July, and August) was 3,880 kg from sub-watershed-1, 7,981 kg from subwatershed-6, and 18,023 kg from sub-watershed-7. Total TSS leaving from the DRC watershed in three months was 221, 440 kg (Table 4). Sub-watershed-7 was contributing the major portion of TSS that passed through the DRC watershed. Compared to other months, highest amount of TSS moved through the system in May. Primarily cause of this is the high rate of soil erosion during that time.

Table 3. Phosphorus load in DRC watershed.

Phosphorus load in Kg				
	May	July	August	Total P from each watershed
Sub-watershed-1	22	21	16	59
Sub-watershed-6	74	170	0	244
Sub-watershed-7	38	17	0	55
Total P from each month	134	208	16	
			Total phosphorus from DRC in three months	594

Table 4. TSS load in DRC watershed.

TSS load in Kg				
	May	July	August	Total TSS from each watershed
Sub-watershed-1	3,165	3,778	4,696	11,639
Sub-watershed-6	7,707	13,691	2,545	23,943
Sub-watershed-7	49,002	2,738	2,329	54,069
Total TSS from each month	59,874	20,207	9,570	
			Total TSS from DRC in three months	221,440

Sub-watershed-6 was the main source of nutrients (nitrate and phosphorus) during the study period. Sub-watershed-6 received runoff both from agricultural and urban areas. Therefore it might have collected nitrate and phosphorus from multiple sources. Sub-watershed-7 was the main source of TSS. This sub-watershed received runoff mainly from the agricultural areas. Therefore, soil erosion due to agricultural activities must have contributed suspended sediments to the stream channels. Total suspended sediment load leaving from the DRC was more than the combined load of the three sub-watersheds. This excess TSS was coming from the areas of the watershed that were not included in the sub-watersheds (Figure 20 and 21). These areas are mostly downstream urban areas. Thus, urban area contributed a significant amount of TSS.

The estimated nitrogen load was relatively higher than what Tavener and Iqbal (2003) calculated in watersheds from northeastern Iowa. In their study, the average nitrate was 5 mg/l while in this study found 17.64 mg/l as the average nitrate concentration in water. Higher nitrate concentration could be due to the dry weather that is not favorable for denitrification and infiltration of nitrate to the subsurface (Libra et al., 2004). On the other hand, phosphorus load was comparatively lower than what Tavener and Iqbal (2003) had calculated. They calculated average phosphorus load at 400 µg/l, but in this study the average phosphorus concentration in stream water was 68.5 µg/l. This difference might be due to the dry climate and lack of precipitation as phosphorus is mainly transported with soil erosion (Iqbal et al., 2006; Libra et al., 2004).

According to Libra et al., (2004) total nitrogen input from various sources (mainly as fertilizers and soil nitrogen) in Cedar River watershed in the upstream area of Waterloo (including the study area) is 245 lb/acre or 111.13 kg/acre annually. The area of DRC watershed is 61.05 km^2 or 15,086 acre, which means this watershed receives about 1.68x10^6 kg nitrogen annually. Nitrogen harvested by crops was estimated to be about 40% (Libra et al., 2004) which means that approximately 6.8x10^5 kg nitrogen was harvested by crops from this watershed during the growing season. In three months of this study about 2.5x10^5 kg nitrate (NO_3^-) or 5.5x10^4 kg nitrogen (NO_3^--N) left the watershed through the stream, which is about 3.3 % of the total nitrogen that was received in this watershed. Annually statewide reported nitrogen loss through streams was 5% (Libra et al., 2004). Thus the 3.3% nitrogen loss in three months of this study was expected. It also shows that most of the nitrogen that transported by streams leaves the watershed during agricultural activities. Rest of the nitrogen was lost in various processes like volatilization, denitrification, and as soil nitrogen (Libra et al., 2004).

Annul total phosphorus input from various sources (mostly as fertilizers and manure) in Cedar River watershed in the upstream area of Waterloo (including the study area) was calculated as 14.8 lb/acre or 6.7 kg/acre (Libra et al., 2004). Which means that the watershed receives about 1.01x10^5 kg P annually. Phosphorus uptake by crops was estimated at 88% (Libra et al., 2004), indicating that about 8.08x10^4 kg P was used by crops (corn, in particular). In the three months of the study, about 594 kg of total P left through the stream, which is about 0.6% of the total annual input. Statewide P loss by streams was reported to be 4% (Libra et al., 2004). Less phosphorus output by the stream during this study could be the result of dry weather as indicated before.

CHAPTER 5

SUMMARY AND CONCLUSIONS

In this study, agricultural soil showed high levels of nitrate and phosphorus but relatively low levels of chloride compared to other hydrologic units. On the other hand, groundwater samples from agricultural areas had low nitrate and phosphorus. Urban soil had relatively low nitrate and phosphorus compared to agricultural soil. On the contrary, groundwater beneath urban areas had high nitrate and phosphorus compared to agricultural areas. Agricultural areas were the main source of TSS, nitrate, chloride and phosphorus in most surface water bodies. In some cases however, urban areas supplied significant amounts of these nutrients and other pollutants. Within the urban areas, soil nitrate, phosphorus, and chloride concentrations were relatively high in the central part of the unit compared to the periphery. Agricultural areas didn’t show any spatial variations in soil nitrate, phosphorus, and chloride concentrations. Both agricultural and urban soil had similar kinds of organic matter percentages.

In the wetland, soil had nitrate concentrations below detection but had high phosphorus in the month of May compared to other units. Open water in wetland had low nitrate, phosphorus and chloride compared to the other surface water bodies. There were significant differences between the inlet points and the outlet point of the wetland in terms of TDS and dissolved nitrate, phosphorus, and chloride. In the inlet points, these concentrations were mostly higher compared to the outlet point, indicating active recycling of nutrients within the wetland. In prairie, most of the time there was no nitrate but it had high phosphorus in water as well as in soil. TDS values in the prairie were the lowest among all hydrologic units. No nitrate and very low TDS indicate pristine soil and active recycling of nutrients in prairie. Some samples showed high total phosphorus. This is due to the long term accumulation of phosphorus by its strong adsorption to soil. Phosphorus does not easily go into solution because of its hydrophobicity. This restricts quick removal of P from hydrologic systems, unlike nitrogen.

In stream bank soil, nitrate and phosphorus were relatively low but chloride was the highest among all units. These nutrients were found in higher concentrations in the agricultural areas compared to the urban areas. In addition, nitrate, phosphorus, chloride, TDS and TSS values were the highest in stream water compared to other surface water bodies. Stream water had a sudden drop in nitrate after July indicating that they were primarily derived from agricultural activities. All units showed relative fluctuations in nutrient levels throughout the study period. This indicates that the nutrients were actively moving through the watershed.

Sub-watershed-6 received water from both urban and agricultural areas and was the main contributor of nitrate and phosphorus to the watershed in general. The highest amount of nitrate and phosphorus was delivered from this sub-watershed in the month of May and July, respectively. Though both were coming from the same general sources, phosphorus took more time to be incorporated to the system compared to nitrate. This is because phosphorus is less mobile in water than nitrate. The main source of TSS was sub-watershed-7, which delivered about 54,000 kg of TSS to DRC. This sub-watershed received water mainly from the agricultural areas. More than 50% of the total TSS load was delivered during the month of May, which reaffirms the link between agricultural activities and TSS.

Although agricultural soil had the highest amount of nitrate and phosphorus, sub-watershed-7, which received water mainly from the agricultural areas, delivered less nitrate and phosphorus compared to sub-watershed-6. This might be because of the vertical infiltration rates. The average infiltration rate in agricultural areas was the highest among all hydrologic units. High infiltration rate might have caused rapid vertical movement of nutrients in sub-watershed-7. Fluctuations of soil nitrate and phosphorus at 6 and 12 inch depths also support the idea of vertical loss of nutrients. Thus, high soil nutrients and high infiltration rates made the agricultural areas more prone to vertical loss of nutrients from the surface during rain events.

Though agricultural areas are more vulnerable to vertical input of nutrients, groundwater from these areas had low nitrate and phosphorus. This could be due to dilution of nutrients by excess rainwater infiltrating from the surface. Within this watershed, agricultural areas are located in the upstream areas and the urban part is located in the downstream areas. Thus, it is possible that contaminants coming from the upstream agricultural areas are eventually lost by shallow subsurface flow to downstream urban areas. In this process of transportation, although urban and agricultural areas are both working as sources of contaminants, groundwater in urban areas seems to show higher levels of dissolved nutrients.

All hydrologic units were very active and were interacting with one another during the study period. Active nutrient recycling was observed in all units within the watershed. This study only gives a short term scenario of nutrient transportation within the small watershed of DRC. As this study was conducted in a dry year, it will be very much useful to repeat the study in relatively wet year to see the consistence of the results. Besides, long term study is needed to understand the exact role of the hydrologic units in terms of temporal and spatial accumulation and release of nutrients. More in-depth research on groundwater is needed to understand its regional migration in the subsurface.

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APPENDIX A

SAMPLING LOCATIONS AND TYPES OF SAMPLES COLLECTED

No	Hydrologic Units	Sample ID	Latitude	Longitude	Samples Collected
1	Prairie	P-1	42.5931	-92.5536	Soil, Water
2	Prairie	P-2	42.5923	-92.5521	Soil, Water
3	Prairie	P-3	42.5931	-92.5513	Soil, Water
4	Rural	R-1A	42.5418	-92.5131	Soil
5	Rural	R-1	42.5392	-92.513	Soil, Water
6	Rural	R-2	42.4764	-92.5336	Soil, Water
7	Rural	R-3	42.5136	-92.512	Soil, Water
8	Rural	R-4	42.5162	-92.5238	Soil, Water
9	Rural	R-5	42.4685	-92.479	Soil, Water
10	Rural	R-6	42.4965	-92.485	Soil
11	Rural	R-7	42.5091	-92.4946	Soil
12	Rural	R-8	42.4693	-92.4693	Soil
13	Stream	S-1	42.5192	-92.461	Soil, Water
14	Stream	S-2	42.4966	-92.4853	Water
15	Stream	S-3	42.5276	-92.4751	Soil, Water
16	Stream	S-4	42.5093	-92.4948	Water
17	Stream	S-5	42.4877	-92.4623	Soil, Water
18	Stream	S-6	42.5061	-92.4465	Soil, Water
19	Stream	S-7	42.5083	-92.4552	Soil, Water
20	Stream	S-8	42.5253	-92.4411	Soil, Water
21	Stream	S-9	42.5257	-92.433	Soil, Water
22	Stream	S-11	42.4694	-92.469	Water
23	Stream	S-12	42.4849	-92.4949	Soil, Water
24	Stream	S-13	42.5399	-92.4498	Soil, Water
25	Urban	U-1	42.5115	-92.4152	Soil
26	Urban	U-2	42.5336	-92.4772	Soil
27	Urban	U-3	42.5218	-92.4559	Soil
28	Urban	U-4	42.5221	-92.4688	Soil
29	Urban	U-5	42.4899	-92.4672	Soil
30	Urban	U-6	42.4977	-92.4476	Soil
31	Urban	U-7	42.5058	-92.4544	Soil
32	Urban	U-8	42.5095	-92.4701	Soil
33	Urban	U-9	42.5083	-92.4554	Water
34	Urban	U-10	42.5127	-92.4584	Water
35	Urban	U-11	42.5163	-92.4144	Water
36	Urban	U-12	42.5281	-92.4667	Water
37	Urban	U-13	42.4988	-92.4143	Water
38	Wetland	W-1	42.5201	-92.468	Soil, Water
39	Wetland	W-2	42.5208	-92.4706	Water
40	Wetland	W-3	42.5216	-92.4708	Soil, Water
41	Wetland	W-4	42.5215	-92.467	Soil, Water
42	Wetland	W-5	42.5215	-92.4702	Soil, Water
43	Wetland	W-6	42.5201	-92.4661	Soil, Water

APPENDIX B

SOIL ORGANIC MATTER PERCENTAGES IN DIFFERENT HYDROLOGIC UNITS

Sample ID	Depth in inch	Percentage of OM			
		May	June	July	October
S-1	0	7.18	8.24	7.77	5.48
	6	7.50	6.76	6.63	3.59
	12	7.88	6.72	6.95	6.70
S-2	0	8.24	7.79	6.37	6.47
	6	6.89	8.19	6.01	6.57
	12	7.76	8.92	6.48	8.08
S-3	0	5.33	7.26	3.23	6.16
	6	4.09	5.80	2.56	4.52
	12	4.37	5.66	2.66	3.55
S-4	0	14.53	5.89	5.84	5.56
	6	6.61	4.99	5.05	5.10
	12	6.56	5.03	5.67	5.85
S-5	0	8.73	7.62	8.17	8.03
	6	7.49	5.77	7.56	6.78
	12	8.63	5.64	2.68	6.13
S-6	0	6.54	5.50	6.28	3.74
	6	5.88	4.93	5.20	3.82
	12	6.35	4.85	4.45	3.85
S-7	0	4.76	2.18	2.27	2.15
	6	4.67	3.04	4.68	3.49
	12	3.86	4.07	4.06	3.93
S-8	0	6.29	7.51	5.08	3.41
	6	6.59	3.77	6.16	3.93
	12	5.52	4.28	5.53	4.61
S-9	0	6.85	5.35	13.46	8.49
	6	5.86	6.72	7.22	7.41
	12	5.96	6.44	6.26	6.94
S-11	0	9.11	8.36	9.33	8.06
	6	8.82	8.33	8.96	8.60
	12	7.73	8.27	10.50	9.54
S-12	0	6.19	5.84	3.03	4.19
	6	3.31	2.89	2.24	2.61
	12	3.89	4.53	2.64	3.35
S-13	0	3.21	3.29	1.92	2.44
	6	1.71	2.74	1.31	1.32
	12	1.31	3.65		1.59
U-1	0	6.74	5.61	7.42	4.25
	6	5.47	7.22	5.82	3.60
	12	3.85	6.55	6.06	4.29
U-2	0	7.75	8.73	7.33	5.61
	6	4.97	6.77	5.89	4.63
	12	3.91	5.05	4.84	4.03
U-3	0	11.26	9.80	8.74	9.93
	6	7.97	9.70	8.43	8.66
	12	9.80	8.71	7.19	8.35
U-4	0	9.25	11.75	10.81	9.31
	6	3.14	10.40	10.22	9.29
	12	2.22	10.08	10.00	7.56
U-5	0	4.07	6.70	5.46	5.33
	6	3.89	7.05	5.96	2.38
	12	5.92	7.04	5.76	6.06
U-6	0	5.60	28.55	4.84	5.71
	6	5.61	4.94	4.77	5.13
	12	6.50	5.62	4.87	4.81
U-7	0	8.61	7.63	6.83	6.56
	6	6.72	6.16	4.98	5.25
	12	3.27	4.36	4.45	5.24
U-8	0	6.90	6.94	6.43	5.86
	6	4.67	5.07	4.54	4.67
	12	4.35	5.29		5.23
R-1(A)	0	7.54	8.62	8.00	7.30
	6	7.48	7.43	6.88	6.45
	12	7.25	7.71	7.13	6.91
R-1	0	6.16	7.46	6.47	6.23
	6	5.44	5.54	5.57	5.57
	12	5.29	5.02	4.27	5.27
R-2	0	7.36	6.92	6.66	5.68
	6	7.07	6.74	6.01	5.39
	12	6.49	6.57	6.22	4.28
R-3	0	7.10	6.74	8.16	8.23
	6	8.62	7.62	10.20	8.11
	12	6.22	7.35	6.75	7.69
R-4	0	6.43	5.91	5.72	6.79
	6	7.36	5.77	6.08	6.15
	12	6.35	5.66	5.75	4.99
R-5	0	9.31		8.53	8.44
	6	8.92	7.65	7.10	7.14
	12	6.72	6.61	6.12	6.30
R-6	0	8.24	7.79	6.37	6.47
	6	6.89	8.19	6.01	6.57
	12	7.76	8.92	6.48	8.08
R-7	0	14.53	5.89	5.84	5.56
	6	6.61	4.99	5.05	5.10
	12	6.56	5.03	5.67	5.85
R-8	0	9.11	8.36	9.33	8.06
	6	8.82	8.33	8.96	8.60
	12	7.73	8.27	10.50	9.54
W-1	0	6.82	6.45	15.04	8.75
	6	5.43	3.61	5.23	4.49
	12	7.26	2.76	3.81	3.14
W-3	0	5.46	1.73	3.01	
	6	0.88	1.62	1.37	
	12	0.67	0.48	0.65	
W-4	0	5.72	1.77	1.36	2.58
	6	2.82	1.82	1.85	1.88
	12	2.18	2.02	2.02	2.11
W-5	0	0.98	0.59	0.89	0.90
	6	1.52	0.60	0.75	0.70
	12	0.99	0.87	0.64	0.52
W-6	0	5.19	3.78	4.34	4.79
	6	4.64	3.48	3.66	4.21
	12	4.44	1.54	1.92	2.33
P-1	0	15.57	8.49		17.72
	6	6.03	7.08		8.12
	12	4.75	5.76		5.86
P-2	0	6.91	4.97		5.57
	6	1.80	2.37		2.96
	12	4.97	2.38		2.24
P-3	0	4.75	3.65		4.91
	6	12.40	1.93		1.96
	12	1.01	1.56		1.16

APPENDIX C

SOIL NITRATE CONCENTRATIONS IN DIFFERENT HYDROLOGIC UNITS

Sample ID	Depth in inch	Nitrate (mg/kg)			
		May	June	July	October
S-1	0	n.a	46.13	35.09	n.a
	6	n.a	47.89	44.45	n.a
	12	n.a	44.05	43.70	59.95
S-3	0	36.72	47.91	n.a	41.15
	6	31.95	31.54	n.a	32.24
	12	n.a	n.a	n.a	n.a
S-5	0	34.70	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
S-6	0	n.a	n.a	36.71	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
S-7	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
S-8	0	n.a	n.a	35.45	64.30
	6	30.39	n.a	n.a	45.45
	12	n.a	n.a	34.28	n.a
S-9	0	n.a	n.a	52.20	43.58
	6	n.a	66.93	n.a	n.a
	12	32.99	n.a	n.a	38.84
S-12	0	37.55	35.64	104.98	127.03
	6	n.a	n.a	41.79	50.06
	12	n.a	46.38	n.a	63.74
S-13	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
U-1	0	48.60	n.a	76.14	n.a
	6	36.59	43.20	34.25	n.a
	12	22.61	n.a	n.a	n.a
U-2	0	18.06	n.a	76.45	190.47
	6	15.11	n.a	54.31	51.85
	12	0.00	n.a	52.35	46.82
U-3	0	32.79	n.a	44.61	40.24
	6	36.37	n.a	58.59	0.00
	12	31.11	n.a	46.34	0.00
U-4	0	20.73	46.91	105.00	39.86
	6	16.14	n.a	81.95	n.a
	12	6.95	n.a	47.49	n.a
U-5	0	0.00	43.54	n.a	n.a
	6	0.00	33.13	n.a	n.a
	12	0.00	n.a	n.a	n.a
U-6	0	20.55	34.84	96.58	n.a
	6	63.75	0.00	43.72	n.a
	12	24.17	0.00	n.a	n.a

Sample ID	Depth in	Nitrate (mg/kg)			
		May	June	July	October
U-7	0	17.81	32.41	101.24	63.34
	6	n.a	n.a	62.66	36.68
	12	n.a	n.a	46.90	42.57
U-8	0	n.a	n.a	n.a	n.a
	6	8.30	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
R-1(A)	0	19.62	70.00	526.18	213.78
	6	28.52	81.45	58.97	158.09
	12	34.15	72.76	48.55	192.64
R-1	0	96.99	32.75	98.55	180.50
	6	29.81	47.91	38.49	35.37
	12	28.16	35.88	0.00	49.15
R-2	0	18.69	65.32	62.26	47.77
	6	n.a	59.39	39.99	n.a
	12	n.a	n.a	60.41	n.a
R-3	0	436.57	156.55	275.87	144.17
	6	206.84	203.28	183.73	47.73
	12	289.61	69.96	105.71	36.98
R-5	0	60.74	0.00	119.84	89.80
	6	n.a	67.88	92.38	101.85
	12	n.a	46.82	60.83	n.a
R-6	0	n.a	0.00	72.31	81.91
	6	n.a	53.26	34.12	n.a
	12	n.a	66.21	51.83	n.a
R-4	0	70.35	0.00	87.10	38.85
	6	27.03	44.90	65.47	37.63
	12	30.51	n.a	40.44	n.a
R-7	0	109.42	51.69	252.31	153.14
	6	33.77	55.30	91.40	101.21
	12	42.89	n.a	44.20	84.19
R-8	0	59.93	n.a	216.89	78.02
	6	42.14	56.69	105.62	68.67
	12	39.90	30.84	50.28	65.23
P-1	0	n.a	1.08		n.a
	6	n.a	1.11		n.a
	12	n.a	0.00		n.a
P-2	0	n.a	1.40		n.a
	6	n.a	0.00		n.a
	12	n.a	1.15		n.a
P-3	0	n.a	1.11		n.a
	6	n.a	1.08		n.a
	12	n.a	0		n.a

APPENDIX D

SOIL TOTAL PHOSPHORUS CONCENTRATIONS IN DIFFERENT HYDROLOGIC UNITS

Sample ID	Depth in inch	Total Phosphorus (µg/g)		
		May	July	October
S-1	0	29.6	10.5	n.a
	6	36.7	0.4	14.5
	12	62.1	5.0	0.7
S-3	0	n.a	n.a	n.a
	6	n.a	n.a	n.a
	12	n.a	n.a	n.a
S-5	0	17.3	1.6	10.9
	6	3.4	13.9	5.3
	12	5.4	7.1	1.5
S-6	0	30.3	n.a	n.a
	6	16.3	41.8	n.a
	12	33.0	41.8	15.1
S-7	0	10.4	14.2	11.9
	6	36.5	12.0	14.1
	12	12.3	24.7	19.0
S-8	0	n.a	n.a	n.a
	6	n.a	n.a	n.a
	12	n.a	n.a	n.a
S-9	0	0.5	n.a	n.a
	6	n.a	10.0	1.8
	12	1.8	0.7	13.5
S-12	0	14.4	8.0	5.0
	6	15.2	10.7	9.5
	12	14.8	0.7	3.7
S-13	0	n.a	n.a	n.a
	6	4.6	3.3	n.a
	12	n.a		n.a
U-1	0	64.2	20.2	62.3
	6	49.2	7.7	1.8
	12	n.a	5.0	-0.5
U-2	0	103.4	30.3	13.6
	6	58.1	30.5	0.0
	12	181.5	11.0	n.a
U-3	0	173.6	76.9	49.3
	6	277.8	30.9	9.0
	12	257.9	30.5	46.6
U-4	0	52.9	36.9	3.9
	6	3.7	35.5	15.4
	12	283.7	28.6	5.3
U-5	0	n.a	27.8	15.4
	6	n.a	22.8	12.0
	12	49.2	20.2	29.7
U-6	0	242.9	26.3	43.6
	6	121.0	17.8	26.9
	12	212.2	71.9	48.0
U-7	0	284.9	88.4	79.4
	6	183.1	52.6	70.0
	12	68.1	45.2	30.7
U-8	0	n.a	14.4	13.6
	6	5.3	2.0	14.4
	12	n.a		27.4
R-1(A)	0	386.9	53.7	39.7
	6	155.9	18.1	39.7
	12	65.5	21.6	14.3
R-1	0	179.8	58.2	76.1
	6	273.1	34.8	59.5
	12	142.3	57.5	18.2
R-2	0	136.6	73.1	60.3
	6	373.6	63.9	41.2
	12	67.2	108.3	17.7
R-3	0	42.1	7.5	7.5
	6	76.7	12.3	16.4
	12	81.7	10.3	2.7
R-4	0	59.7	36.1	98.2
	6	79.5	75.8	57.8
	12	80.6	62.5	32.6
R-5	0	360.1	66.4	78.1
	6	422.6	80.2	110.7
	12	211.7	38.4	210.4
R-6	0	114.6	90.3	46.3
	6	17.5	74.8	53.4
	12	32.3	57.7	18.6
R-7	0	13.0	33.5	22.3
	6	22.5	19.3	11.1
	12	18.4	73.3	6.1
R-8	0	50.6	28.8	26.4
	6	43.4	28.4	25.0
	12	0.1	27.0	58.8
W-1	0	24.0	5.2	3.7
	6	27.2	16.7	n.a
	12	40.3	18.0	0.6
W-3	0	290.6	127.5	
	6	635.1	95.1	
	12	813.6	22.9	
W-4	0	910.2	5.5	n.a
	6	165.2	1.7	n.a
	12	19.6	2.7	n.a
W-5	0	30.9	1.3	5.2
	6	6.5	12.9	8.7
	12	17.9	3.4	n.a
W-6	0	1.1	1.3	0.4
	6	29.1	5.1	1.9
	12	51.6	17.2	10.3
P-1	0	72.5		99.0
	6	157.5		249.3
	12	221.0		190.4
P-2	0	161.2		72.2
	6	209.4		96.1
	12	366.6		114.6
P-3	0	136.5		52.6
	6	239.4		65.0
	12	153.4		76.8

APPENDIX E

SOIL CHLORIDE CONCENTRATIONS IN DIFFERENT HYDROLOGIC UNITS

Sample ID	Depth in inch	Chloride (mg/kg)				Sample ID	Depth in inch	Chloride (mg/kg)			
		May	June	July	October			May	June	July	October
S-1	0	n.a	35.55	98.17	n.a	R-1(A)	0	8.59	n.a	n.a	142.395
	6	n.a	34.53	139.29	n.a		6	8.42	21.41	n.a	n.a
	12	n.a	31.53	232.38	n.a		12	10.01	n.a	n.a	n.a
S-3	0	n.a	42.81	27.28	n.a	R-1	0	48.28	n.a	n.a	114.912
	6	n.a	50.94	39.72	38.44		6	14.88	n.a	n.a	n.a
	12	n.a	25.35	23.02	n.a		12	8.49	n.a	n.a	n.a
S-5	0	n.a	95.41	57.55	36.86	R-2	0	8.31	n.a	n.a	n.a
	6	n.a	83.35	68.47	320.03		6	16.72	23.63	20.49	n.a
	12	n.a	76.53	98.53	222.56		12	22.49	27.78	19.75	n.a
S-6	0	n.a	n.a	n.a	n.a	R-3	0	61.06	0.00	46.23	32.346
	6	n.a	n.a	n.a	n.a		6	19.50	21.27	19.92	19.947
	12	n.a	n.a	n.a	n.a		12	18.62	22.82	n.a	n.a
S-7	0	250.00	43.54	171.26	n.a	R-4	0	8.97	n.a	n.a	n.a
	6	150.00	90.12	285.00	n.a		6	13.50	n.a	n.a	n.a
	12	120.00	97.01	135.71	n.a		12	18.88	n.a	n.a	n.a
S-8	0	n.a	n.a	n.a	n.a	R-5	0	10.34		n.a	63.333
	6	n.a	n.a	n.a	n.a		6	15.19	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a		12	11.96	n.a	n.a	n.a
S-9	0	n.a	n.a	21.33	n.a	R-6	0	n.a	29.34	n.a	n.a
	6	n.a	n.a	n.a	n.a		6	n.a	36.33	150.00	n.a
	12	n.a	n.a	n.a	n.a		12	n.a	37.49	130.00	n.a
S-12	0	n.a	n.a	n.a	n.a	R-7	0	n.a	30.93	n.a	n.a
	6	n.a	n.a	n.a	n.a		6	n.a	31.96	n.a	n.a
	12	n.a	n.a	n.a	n.a		12	n.a	30.45	n.a	n.a
S-13	0	n.a	27.83	16.71	n.a	R-8	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	22.08		6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	16.77		12	n.a	n.a	n.a	n.a
U-1	0	11.86	n.a	28.67	n.a	W-1	0	19.32	48.18	33.99	n.a
	6	9.03	n.a	25.76	19.48		6	17.28	90.38	69.22	n.a
	12	n.a	n.a	n.a	n.a		12	45.45	115.54	105.63	n.a
U-2	0	12.03	20.77	22.56	38.54	W-3	0	n.a	n.a	n.a	
	6	16.00	21.76	23.03	31.44		6	n.a	n.a	n.a	
	12	10.47	30.76	21.55	47.44		12	n.a	n.a	n.a	
U-3	0	n.a	n.a	n.a	19.40	W-4	0	n.a	n.a	23.84	n.a
	6	n.a	n.a	n.a	n.a		6	n.a	n.a	0.00	n.a
	12	n.a	n.a	n.a	n.a		12	n.a	n.a	18.73	n.a
U-4	0	9.88	n.a	n.a	n.a	W-5	0	n.a	18.41	101.41	82.15
	6	15.15	n.a	n.a	n.a		6	n.a	n.a	n.a	n.a
	12	19.16	n.a	n.a	n.a		12	n.a	n.a	n.a	n.a
U-5	0	9.79	n.a	30.33	41.05	W-6	0	n.a	75.68	68.65	63.08
	6	n.a	n.a	22.79	26.62		6	38.47	71.36	0.00	31.79
	12	n.a	n.a	20.72	20.03		12	41.18	41.96	41.80	50.60
U-6	0	n.a	n.a	n.a	n.a	P-1	0	n.a	33.82		n.a
	6	n.a	n.a	n.a	n.a		6	n.a	33.01		n.a
	12	n.a	n.a	22.81	n.a		12	n.a	32.70		n.a
U-7	0	n.a	n.a	26.12	n.a	P-2	0	n.a	50.74		n.a
	6	n.a	n.a	n.a	n.a		6	n.a	45.76		n.a
	12	n.a	n.a	n.a	n.a		12	n.a	n.a		n.a
U-8	0	11.24	19.67	66.02	24.69	P-3	0	n.a	33.99		n.a
	6	48.50	52.93	61.13	41.12		6	8.83	33.12		n.a
	12	63.53	57.84	n.a	75.22		12	n.a	32.81		n.a

APPENDIX F

SOIL SULFATE CONCENTRATIONS IN DIFFERENT HYDROLOGIC UNITS

Sample ID	Depth in inch	Sulfate (mg/kg)			
		May	June	July	October
S-1	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	20.92
S-3	0	24.72	n.a	22.79	n.a
	6	20.57	n.a	22.78	n.a
	12	n.a	n.a	22.67	n.a
S-5	0	n.a	43.57	35.38	24.54
	6	n.a	39.29	38.45	135.97
	12	n.a	38.76	57.57	142.78
S-6	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
S-7	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	20.58	n.a
	12	n.a	n.a	n.a	n.a
S-8	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
S-9	0	n.a	n.a	21.86	35.29
	6	n.a	n.a	n.a	21.08
	12	n.a	n.a	n.a	n.a
S-12	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
S-13	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a		n.a
U-1	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
U-2	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
U-3	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
U-4	0	n.a	n.a	n.a	n.a
	6	73.31	n.a	n.a	n.a
	12	67.55	n.a	n.a	n.a
U-5	0	18.02	n.a	n.a	n.a
	6	20.04	n.a	n.a	n.a
	12	48.00	n.a	n.a	n.a
U-6	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
U-7	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
U-8	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	12.57	n.a		n.a

Sample ID	Depth in inch	Sulfate (mg/kg)			
		May	June	July	October
R-1(A)	0	19.07	n.a	n.a	n.a
	6	24.28	n.a	n.a	n.a
	12	27.70	n.a	n.a	n.a
R-1	0	70.08	n.a	n.a	n.a
	6	27.90	n.a	n.a	n.a
	12	30.30	n.a	n.a	n.a
R-2	0	12.65	n.a	n.a	n.a
	6	27.02	n.a	n.a	n.a
	12	56.97	n.a	n.a	n.a
R-3	0	96.48	n.a	n.a	n.a
	6	45.37	n.a	n.a	n.a
	12	53.43	n.a	n.a	n.a
R-4	0	16.77	n.a	n.a	n.a
	6	31.21	n.a	n.a	n.a
	12	33.30	n.a	n.a	n.a
R-5	0	22.49	n.a	n.a	56.38
	6	37.74	n.a	23.70	25.40
	12	47.24	n.a	30.29	25.69
R-6	0	n.a	n.a	n.a	26.84
	6	n.a	n.a	n.a	25.19
	12	n.a	n.a	n.a	0.00
R-7	0	n.a	n.a	20.69	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
R-8	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
W-1	0	17.64	n.a	n.a	n.a
	6	12.24	n.a	n.a	n.a
	12	93.40	n.a	n.a	n.a
W-3	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
W-4	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
W-5	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
W-6	0	n.a	n.a	n.a	n.a
	6	n.a	n.a	n.a	n.a
	12	n.a	n.a	n.a	n.a
P-1	0	23.21	n.a		32.77
	6	16.22	n.a		n.a
	12	19.65	n.a		n.a
P-2	0	20.23	n.a		n.a
	6	17.85	n.a		n.a
	12	16.15	n.a		n.a
P-3	0	24.50	n.a		n.a
	6	26.55	n.a		n.a
	12	16.31	n.a		n.a

APPENDIX G

SURFACE WATER DATA

Sample ID	May										
	On-site Parameters						Lab Analysis				
	Tem. (°C)	pH	TDS (mg/l)	Conductivity (µS/cm)	DO (mg/l)	BOD (mg/l)	TSS (mg/l)	Chloride (mg/l)	Nitrate (mg/l)	Sulfate (mg/l)	Total Phosphorus (µg/l)
S-1	18.1	8.24	322	466	9.45	2.33	3.17	11.25	2.19	18.86	22.10
S-2	20.3	8.13	366	533	10.53	2.33	6.17	22.90	55.82	12.75	33.33
S-3	18.1	8.09	405	588	9.21	2.05	1.33	57.20	6.85	24.93	36.14
S-4	20.6	8.14	370	530	9.62	2.54	26.17	21.20	51.46	13.54	19.29
S-5	20.4	8.38	348	505	8.8	2.12	1.17	47.12	16.63	20.71	22.10
S-6	18.2	8.14	456	656	8.4	1.87	2	63.75	44.05	24.44	19.29
S-7	18.9	8.09	354	515	8.75	1.45	28.17	37.94	21.41	25.20	22.10
S-8	16.5	8.34	401	576	9.24	1.64	27.17	38.22	21.23	25.33	55.80
S-9	21.3	8	367	532	8	0.98	4.33	29.45	47.08	23.63	72.65
S-11	18.8	8.14	411	593	9.09	3	6	33.06	87.69	15.83	52.99
S-12	18.7	7.98	373	547	9.15	1.35	14.5	23.33	59.10	12.66	24.90
S-13	19.2	8.1	359	512	7.88	2.54	28.45	28.04	54.76	23.62	120.40
June											
S-1	13.1	8.2	299	432	9.52	2.03	1.44	14.86	2.31	18.86	
S-2	12.8	8.28	380	352	9.99	2.36	6.88	23.00	48.01	14.31	
S-3	13.9	8.35	250	362	8.53	1.95	2.23	18.99	4.17	17.53	
S-4	12.6	8.25	386	560	8.42	0.74	4.56	26.01	40.52	14.98	
S-5	13.9	8.43	360	533	9.53	2.87	3.5	47.32	17.98	21.46	
S-6	13.3	8.43	364	529	9.13	2.03	8.54	64.11	18.94	27.68	
S-7	17.3	8.22	366	528	8.04	2.02	22.25	24.61	11.77	17.95	
S-8	13	8.3	283	411	9.14	2.05	6.35	32.09	11.26	18.10	
S-9	13.6	8.6	248	433	8.54	1.84	10.25	33.72	19.30	19.08	
S-11	11.1	8.1	430	625	9.66	3.02	4.55	36.32	79.76	16.71	
S-12	12	8.11	390	570	9.58	1.8	12.25	23.60	52.06	13.89	
S-13	13.8	8.45	334	485	8.47	4.66	12.45	29.46	42.02	27.28	
July											
S-1	18.30	8.08	315.00	460.00	8.12	2.78	3.84	6.61	1.63	17.89	22.10
S-2	19.90	8.00	370.00	537.00	4.88	0.82	2.22	23.81	13.50	18.87	50.18
S-3	20.40	7.98	416.00	602.00	7.85	1.54	3.03	40.92	5.27	31.60	67.03
S-4	20.00	7.90	379.00	550.00	7.11	1.50	10.54	27.13	5.45	19.98	64.23
S-5	21.30	8.24	304.00	441.00	7.46	1.65	3.02	52.84	7.68	22.49	36.14
S-6	21.60	8.13	529.00	740.00	6.77	0.98	6.75	115.78	1.78	41.78	83.89
S-7	20.90	8.12	376.00	543.00	7.67	1.65	6.52	30.63	5.08	31.15	41.76
S-8	20.10	8.33	381.00	553.00	8.18	1.00	4.55	32.70	6.39	29.43	38.95
S-9	21.90	8.09	383.00	556.00	7.59	1.65	8.23	30.25	19.28	31.15	100.74
S-11	20.20	8.00	469.00	681.00	7.32	1.45	1.23	72.69	19.77	27.03	64.23
S-12	19.50	8.08	375.00	544.00	6.89	1.60	5.23	12.79	4.11	9.28	173.76
S-13	25.30	8.37	286.00	414.00	11.76	2.02	16.79	30.32	7.51	33.76	89.50

Sample ID	August										
	On-site Parameters						Lab Analysis				
	Tem. (°C)	pH	TDS (mg/l)	Conductivity (µS/cm)	DO (mg/l)	BOD (mg/l)	TSS (mg/l)	Chloride (mg/l)	Nitrate (mg/l)	Sulfate (mg/l)	Total Phosphorus (µg/l)
S-1	16.2	8	289	430	8.99	2.22	5.02	12.45	7.43	13.56	17.64
S-2	18.5	8.25	375	540	6.55	1.02	1.36	12.95	9.74	14.19	n.a
S-3	15.8	8.05	400	575	8.56	2.02	3.44	13.75	10.34	15.01	n.a
S-4	15.7	8.11	384	554	6.56	0.87	2.02	14.60	10.94	15.74	n.a
S-5	19.5	8.25	300	430	9.45	2.89	4.23	15.40	11.47	16.48	n.a
S-6	17.7	8.45	450	601	8.35	1.02	2.01	16.16	11.94	17.26	n.a
S-7	18.3	8.25	370	540	8.45	1.02	4.55	16.62	12.35	17.92	n.a
S-8	18.9	8.4	300	460	8.85	1.23	1.02	19.10	4.05	17.73	n.a
S-9	16.5	8.1	400	601	8.06	1.75	4.55	19.76	4.10	18.26	n.a
S-11	15.5	8.11	450	645	8.53	2.09	4.25	20.39	4.23	18.83	n.a
S-12	17.5	8.01	380	570	7.55	1.75	6.55	21.08	4.37	19.29	n.a
S-13	18.5	8.22	355	520	9.65	3.56	35.96	21.45	4.42	19.66	n.a
October											
S-1	12.3	8.06	129	186	9.2	2.61	0.01	6.37	2.80	9.18	118.12
S-2	13.5	7.82	200	290	8.4	5.41	0.02	12.62	6.67	12.07	393.64
S-3	12.5	7.97	156	227	9.64	2.45	0.01	11.01	10.81	12.42	114.88
S-4	12.4	7.99	149	217	8.67	4.16	0.04	9.93	0.96	16.45	160.26
S-5	13.2	8.11	153	221	9.62	2.92	0.04	16.26	3.82	8.51	95.43
S-6	12.7	8.09	153	222	9.31	2.42	0.03	19.08	2.59	11.79	69.50
S-7	12.2	8.19	182	264	9.23	2.35	0.02	16.31	2.99	16.52	117.59
S-8	12.7	8.17	130	189	9.75	3.15	0.05	12.53	2.77	10.55	120.40
S-9	12.5	8.27	117	169	9.62	3.86	0.03	9.70	2.16	8.91	117.59
S-11	12.5	7.94	360	521	8.12	4.93	0.01	54.07	2.02	29.13	81.08
S-12	11.7	7.91	294	430	8.51	5.99	0.01	16.11	4.13	50.03	482.71
S-13	11	8.72	295	422	11.04	5.8	0.02	28.72	7.36	27.20	64.23
May											
W-1	26.2	7.71	316	459	6.09	0		4.53	0	14.192	68.352
W-2	21.2	7.96	319	527	9.23	3.52		25.63	14.681	22.471	32.722
W-3	22.9	8.35	441	638	11.77	5.1		57.22	6.1332	22.282	88.712
W-4	21.7	8.23	407	591	8.07	4.13		65.92	1.9884	14.264	37.812
W-5	21.6	8.4	336	490	9.73	3.8		36.89	n.a.	28.108	22.542
W-6	24.9	8.28	337	490	11.1	3.1		13.73	3.6695	17.408	22.542
Mid-May											
W-1	27.1	7.79	315	458	6.18	0		3.29	n.a.	13.928	
W-2	22	8.19	390	566	10.27	3.47		27.17	14.429	23.576	
W-3	23	8.16	456	661	12.3	4.88		61.49	3.8264	23.374	
W-4	26	8.55	417	605	16.91	7.38		101.31	n.a.	15.707	
W-5	25.7	8.38	280	408	10.64	4.19		40.05	n.a.	28.846	
W-6	27.5	8.13	308	447	10.12	2.84		6.59	n.a.	15.719	

Sample ID	**June**										
	On-site Parameters						**Lab Analysis**				
	Tem. (°C)	**pH**	**TDS (mg/l)**	**Conductivity (μS/cm)**	**DO (mg/l)**	**BOD (mg/l)**	**TSS (mg/l)**	**Chloride (mg/l)**	**Nitrate (mg/l)**	**Sulfate (mg/l)**	**Total Phosphorus (μg/l)**
W-1	25.1	7.88	316	460	6.09	0		3.29	0.00	14.10	25.09
W-2	21.8	8.15	391	565	7.58	1.05		27.69	12.20	23.83	25.09
W-3	26	8.28	388	563	15.84	5.56		54.69	0.00	22.55	114.16
W-4	22.5	7.55	367	533	13.25	7.96		58.02	0.00	7.98	47.99
W-5	26.5	8.42	258	377	10.28	3.82		41.35	0.00	27.85	63.26
W-6	25.6	8.1	280	407	12.21	4.7		6.89	0.00	15.96	58.17
Mid-june											
W-1	23.6	7.9	325	470	6.12	0		3.12	n.a.	14.96	
W-2	18.3	8.36	400	580	8.97	2.19		29.27	9.53	23.88	
W-3	20.3	7.87	307	446	4.02	0.24		31.06	1.85	19.15	
W-4	25.1	7.81	393	571	8.05	2.23		54.06	n.a.	22.81	
W-5	24.2	8.39	311	451	8.64	5.7		43.38	n.a.	28.35	
W-6	25.7	8.09	313	456	7.97	1.96		5.8136	n.a.	16.208	
July											
W-1	24.5	8.06	308	444	6.22	0		3.77	n.a.	15.42	25.09
W-2	24.1	8.19	437	634	7.09	1.7		27.09	5.85	28.28	98.89
W-3	27.2	8.74	276	403	17.27	13.5		22.76	4.16	14.26	50.54
W-4											
W-5	28.8	8.47	310	449	9.2	3.15		45.93	1.02	28.84	40.36
W-6	26.1	8.24	224	315	10.25	1.55		3.80	n.a.	16.04	22.54
October											
W-1	11.2	8.47	414	596	10.33	2.29		102.76	n.a.	42.02	30.18
W-2											
W-3											
W-4	12.4	8.66	351	505	12.35	5.6		36.77	n.a.	75.90	20.00
W-5	11.6	8.82	323	471	9.65	2.65		48.6552	n.a.	27.402	37.812
W-6	9.3	8.52	327	476	9.9	2.4		31.04	n.a.	24.122	25.087
May											
P-1	17.5	6.74	81	118	1.55	3.2		0.66	n.a.	n.a.	86.167
P-2	16.9	6.12	48	64	1.77	1.4		3.70	n.a.	0.7749	389.022
P-3	18	6.51	35	52	5.9	0.15		0.00	n.a.	n.a.	47.992
October											
P-1	20.5	6.59	125	182	4.33	3.23		0.5764	n.a.	0.8783	65.807
P-2	20.6	6.19	45	72	2.36	1.86		0.00	n.a.	n.a.	55.627
P-3	19.7	6.78	105	147	0.37	0.12		0.90	n.a.	6.8514	55.627

APPENDIX H

GROUNDWATER DATA

Sample ID	May								
	On-site Parameters					Lab Analysis			
	Temperature (°C)	pH	TDS (mg/l)	Conductivity (µS/cm)	DO (mg/l)	Chloride (mg/l)	Nitrate (mg/l)	Sulfate (mg/l)	Total Phosphorus (µg/l)
U-9	14.1	7.79	328	479	1.72	31.47	0.00	13.04	22.54
U-10						56.73	8.39	37.20	25.12
U-11						14.00	40.24	20.54	20.88
U-12						9.42	0.00	17.50	14.40
U-13						49.50	19.67	40.73	24.12
June									
U-9	17.5	7.92	362	526	1.45	32.34	0.00	9.39	25.09
U-10						71.52	10.00	37.31	28.08
U-11						14.45	41.31	21.30	14.40
U-12						10.40	0.00	18.54	17.64
U-13						45.52	19.20	44.46	30.60
July									
U-9	17.80	8.43	190.00	276.00	2.90	32.87	0.00	0.00	27.63
U-10						77.84	11.21	38.10	28.08
U-11						14.49	41.02	21.32	24.12
U-12						10.35	0.00	18.46	14.40
U-13						45.30	21.94	44.20	0.00
May									
R-1		7.80	310.00	452.00	6.76	3.20	5.40	13.90	25.12
R-2	12.3	7.59	332	490	4.02	0.00	0	13.7	25.122
R-3	12.1	7.78	351	520	2.37	10.62	5.56	21.57	28.0774
R-4		7.74	336	487	2.44	7.50	11.2	18.3	42.8544
R-5	15	7.72	318	460	5.67	0.00	3.09	22.21	31.0328
June									
R-1									
R-2	11.9	7.76	329	478	3.1	0.00	0	31.7	22.1666
R-3	10.9	7.93	349	506	8.26	9.72	6.08	21.3	16.2558
R-4									
R-5	11.1	7.83	324	472	6.74	0.00	0	20.23	25.122
July									
R-1	19.1	8.04	307	446	7.01	3.78	5.1	16.02	25.122
R-2	13	7.65	330	480	3.86	0.00	0	14.23	25.122
R-3	11.1	7.9	350	518	6.75	8.22	5.82	21.85	16.2558
R-4	14	7.63	330	450	4.89	7.65	14.32	19.31	45.8098
R-5						1.10	3.6	21.25	19.2112
October									
R-1	19.1	8.04	307	446	7.01	5.42	3.5	21.61	25.122
R-2	17	7.67	320	471	4.49	0.00	0	14.26	31.0328
R-3	11.8	7.96	342	496	2.17	10.22	5.73	22.9	19.2112
R-4	19.2	7.72	336	486	3.2	7.81	14.75	19.2	16.2558
R-5	13.7	7.98	325	472	7.16	1.07	3.78	21.28	19.2112