Evaluation of watershed land use and water quality in Mill Creek, Youngstown, Ohio

by

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Abstract

The Mill Creek Watershed (MCW) is located in Mahoning and Columbiana Counties, Ohio. It is a 47,000 acre sub-watershed of the Mahoning River watershed. The main surface stream is Mill Creek which starts in Fairfield Township, Columbiana County and continues until it reaches the Mahoning River just west of downtown Youngstown. Mill Creek runs through Mahoning County's largest metropolitan park, Mill Creek MetroPark (MCMP). Mill Creek is approximately 39 kilometers long with a mixture of land use types ranging from heavily industrialized and residential to agriculture and mixed forests. The impact of land use practices and aging infrastructure in the Mill Creek Watershed have resulted in various water quality concerns related to human and ecological health. Local water quality issues include bacteria (and other pathogens) from animal waste, combined sewer overflows (CSOs) and failing septic systems; nutrients from urban and agricultural land uses; and sediment loading from erosion and construction. Project objectives are to establish a monitoring program for this watershed. Initial evaluation of MCW monitoring sites, based on specific watershed land uses and inputs (point and non-point) was identified. Twelve sites of concern were selected for water chemical, biological and physical analysis. To establish a control, baseline samples (low flow) were taken during dry periods of rainfall. To assess the effects of land uses in the watershed water samples were collected 24-48 hours after a significant rainfall (>1.9 cm). SPSS analyses were performed using Spearman correlation and ANOVA on SPSS. Soluble reactive phosphate was most prevalent upstream where land use was predominately agricultural. Total and fecal coliforms counts were greatest during the October 21 storm event. During that event, coliform counts were highest, specifically, upstream where agricultural land use dominated and in the Mahoning River where there is larger industrial and residential land use. Precipitation events did not appear to have an influence on any parameters other than total and fecal coliforms. Metals found within the watershed included calcium, potassium, magnesium, sodium, phosphorus, and sulfur. Results of the monitoring program will educate the public on water quality issues and the influence of watershed activity on water quality. Importantly, it will also provide data to Mill Creek MetroParks and the Mahoning County District Board of Health to improve its management of waters coming into and leaving the park.

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Chapter 1 Introduction

From 2015 to 2016, the local media sparked public concern over the water quality within Mill Creek Metropark and its surrounding watershed area. Nutrients, bacteria, and other pollutants have caused unsightly appearance and poor aquatic conditions. One such problem pollutant is Coliform bacteria. Coliform are normally present in the environment because they are found in large numbers in the intestines and fecal material from animals. While many bacteria found in contaminated water are not harmful, some can be pathogenic to humans and cause diseases such as cholera, hepatitis A, dysentery, or typhoid (ND DOH, 2005). Because Mill Creek is a center for recreational activities, such as fishing, boating, and swimming, consumption of contaminated water can be harmful or even fatal to the surrounding population. Fecal material and associated bacteria can be released into the water through land use impacts from nonpoint source runoff and runoff from the river and lake shores as well as point source. Land use involves modifying the natural environment into built environment, which includes settlements, fields, and pastures. Point sources are specific sources of pollution, such as combined sewer overflows. On the contrary, nonpoint sources are sources of pollution that are discharged over a wide land area, not a specific location. Nonpoint source runoff would include, but is not limited to, agriculture, golf courses, and impervious surfaces. Mill Creek is bordered by golf courses, farms, housing developments, industries, wastewater treatment plants (WWTPs), and multiple impervious surfaces, including roads and parking lots. In addition to these land uses, Youngstown houses up to 96 known combined sewer-overflow discharge sites, which release untreated and partially treated wastewater and stormwater into the river (OH EPA, 1996). Sixteen of these sewer-overflows lie within the Mill Creek Watershed area (EPA, 2017). Combined sewer overflows (CSOs) dominate Youngstown's sewer system and discharge wastewater directly into the river during times of intense precipitation. Golf courses, farms, and even housing developments can introduce fertilizers and pesticides containing high concentrations of nitrates and phosphates, which are released into water bodies via surface runoff and can contribute to eutrophication. Water experiencing eutrophication receive a high concentration of nutrients. This can result in an oxygen sag, which is characterized by a reduction of dissolved oxygen due to decomposing bacteria resulting in oxygen levels far below normal, killing aquatic organisms. Runoff, especially after major precipitation events, can largely contribute to water pollution as it is the driving force that gives mobility to the pollutants. Housing developments, impervious surfaces, and farms can also provide nutrients and fecal coliform bacteria due to the runoff of excrement from family pets and livestock. Rising numbers of fecal coliform bacteria can also be caused by the runoff of fecal material from wildlife.

Mill Creek's water quality is impacted by the watershed land use and identifying the sources of pollutants are important in land management. The objective of this study was to establish a monthly baseline of water quality parameters and post rain event water quality parameters in an effort to identify land use that is most prone to cause water contamination. Water quality parameters include fecal and total coliform counts, water temperature, flow, dissolved oxygen, pH, and conductivity, nutrient levels, and biochemical oxygen demand.

Chapter 2 Literature Review

Regulations

The Federal Water Pollution Control Act of 1948 was the first U.S. law set forth to address the hazards of water pollution and work to improve the overall quality of surface waters. This law, amended in 1972, became commonly known as the Clean Water Act. The 1972 amendment regulated pollutant discharges into U.S. waters, gave the Environmental Protection Agency (EPA) the authority to implement pollution control programs, maintained existing requirements to set water quality standards for surface waters, made it illegal to discharge any pollutant from a point source into waters without a permit, funded the construction of wastewater treatment facilities, and recognized a critical need for planning against problems caused by nonpoint source pollution (EPA, 2016). Pollution sources are grouped into two categories: nonpoint and point. Nonpoint sources are spread out over a larger area and are generally harder to pinpoint and regulate due to multiple diffuse sources, whereas point sources originate from a singular, specific output. Nonpoint sources include agricultural land, golf courses, and stormwater while point sources include industrial wastes, wastewater treatment plant discharges, and power plant discharge. Until development of the Clean Water Act, the nation's surface water was unprotected and water quality faced severe degradation. The Mahoning River and Cuyahoga River, commonly known as the river that caught fire, in northeast Ohio have historically been two of the most polluted rivers in Ohio due to unregulated industrial dumping before the enactment of the Clean Water Act, (OH EPA, 1996; NPS 2017). While conservation and remediation progress was initially underway before the passing of the Clean Water Act, these two historical rivers were a constant reminder to not only Ohioans, but to citizens nationwide of how water quality previously was, and reinforced the need to continue striving for future environmental progress.

Water quality reflects the chemical, physical, biological, and radiological characteristics of water. Water pollution means introducing any matter into waters that changes the condition of the water. These pollutants can be caused by natural phenomena, such as volcanic eruptions, or anthropogenic actions. Many pollutants move with water through the aquatic system. Section 40 CFR Part 131 of the Clean Water Act outlines specific regulations on certain pollutants set in place to ensure the safety of surface waters in the United States. Section 307 provides a list of priority pollutants which the EPA must provide water quality criteria for as well as effluent limitations (EPA, 2016). A water quality criteria is a measurable relationship between the quantity of the pollutant or analyte in the water and the potential risk to human health associated with using the water for recreational purposes (NCSU Water Quality Group, 1995). Such standards, known as the maximum contaminant level (MCL), state the maximum amount of each pollutant that is allowed to be present in surface waters without posing a threat to the public. The EPA regulates water quality standards for microorganisms, disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals, and radionuclides, (EPA, 2016).

The Clean Water Act also fostered the creation of wastewater treatment plants as a way to treat contaminated water before discharging it into the environment. These treatment plants are designed to handle millions of gallons of water every day. Residential, industrial, commercial, stormwater, and municipal waters can be sent to wastewater treatment facilities and chemically, biologically, and physically treated to comply with EPA regulations. These regulations are outlined in every plant's National Pollution Discharge Elimination System (NPDES) permit, which allows an industry (wastewater treatment plant) to discharge effluent into receiving surface water bodies, providing the allowable amount of contamination is not exceeded in a given period of time, usually per month and week. An NPDES permit typically contains specific effluent limitations, water quality-based toxic pollutant limitations, whole effluent toxicity requirements (WET), sludge use or disposal criteria, removal efficiency requirements, and requirements that the treatment facility be well operated and maintained (USEPA, 2004). Once the influent enters the plant, it goes through four stages of treatment: preliminary, primary, secondary, and tertiary. Preliminary treatment ensures that larger particles such as paper products, plastic bottles, leaves, and anything else that can be flushed down a toilet or swept into a stormwater grate is filtered out. Normally screens or bar racks are used to accomplish this. In primary treatment, wastewater is deposited into a settling tank where larger particles are able to settle out by gravity at the bottom of the tank. This process removes up to 60% of suspended solids and 20-30% Biochemical Oxygen Demand (BOD) (Yale University, 2017). Secondary treatment is a biological treatment process used to eliminate BOD and further remove solids not settled out during primary treatment. Secondary treatment expels up to 85% of BOD and total suspended solids (Yale University, 2017). The highest level of wastewater treatment is tertiary treatment. Tertiary treatment is used for nutrient removal. This process typically removes phosphorus and nitrogen before discharging the effluent into surface waters. Not all plants contain tertiary treatment due to high costs, so facilities are only required to have up to secondary treatment on site. While wastewater plants are prominent in larger cities with an abundant population, smaller facilities, i.e. package plants, can be used to treat wastewater in less populous communities or rural areas. A positive correlation exists between bacteria levels and residential development in watersheds containing package plants indicating a significantly greater bacteria levels compared to relatively undeveloped watersheds. A watershed is an area of land where all water received from rainfall and stormwater runoff drains to a common outlet (Line, 2013). In watersheds without package plants, there was found to be a linear relationship between fecal coliform levels in baseflow samples and the percentage of impervious surface or residential area, strengthening the claim that coliform levels increase with increasing development (Line, 2013). In addition to coliforms, wastewater treatment facilities are required to monitor and report on many other criteria set forth by the EPA. Common water quality criteria include, but are not limited to, pH, biochemical oxygen demand (BOD) or carbonaceous biochemical oxygen demand (CBOD), solids, nutrients, and coliforms. Once EPA requirements have been met, the plant can legally discharge into a nearby receiving water body, which further dilutes and disperses the effluent as it flows downstream.

Coliform Bacteria

Total coliforms include coliforms that are naturally present in the environment as well as those associated with fecal excrement, which are defined by Fecal coliform bacteria, a subgroup of total coliforms, are naturally found in the digestive tracts of warm blooded animals and are excreted in the feces. These bacteria, normally not a threat to human health, can be used to indicate the likelihood that other harmful bacteria may be present. If a large presence of fecal coliform bacteria is detected, that indicates that there is a potentially higher risk of the presence of harmful bacteria. The harmful bacteria can cause waterborne diseases such as cholera, typhoid fever, and dysentery.

Fecal bacteria can enter the environment through both nonpoint and point sources. Bacteria from agricultural areas, combined sewer overflows (CSOs), stormwater runoff from urban and residential areas, and failed wastewater disposal systems are some of the most common ways bacteria can infiltrate the water system (NCSU Water Quality Group, 1995). Livestock, especially larger animals like cattle, and other wildlife are likely sources of fecal pollution within a predominately agricultural watershed (Webster et al., 2013). Nearby sources of fecal matter have a pronounced impact on water quality over short distances (~12 km) (Twiss et al., 2006).

Bacterial activity can be influenced according to the type of land use, the degree of competition from other microbes, and the availability of nutrients in the system (Williams et al., 2012). While fecal bacteria can only survive for a brief period of time in the aquatic environment, they can persist in large numbers in the sediment. However, disturbances that resuspend this sediment, such as dredging, can potentially decrease fecal coliform counts in water bodies (Mallin, et al., 2000). Fecal bacteria require nutrients for survival. Among the most common nutrients found in aquatic systems are nitrogen, in the forms of nitrate, nitrite, and ammonia, and phosphorus. While naturally found in the ecosystem, large inputs of these nutrients can cause contamination and impact the concentrations of fecal coliform bacteria (Leone et al., 2008). Phosphorus can be bound to sediments where fecal bacteria can persist. Additions of phosphorus, largely organic phosphorus, can sometimes cause significant stimulation of fecal bacteria leading to the concept that extraneous nutrient loading can, at times, impact fecal bacterial populations however, additions of organic and inorganic nitrogen have shown little to no fecal bacterial stimulation (Chudoba et al., 2013).

Nutrients

Ammonia is one of several forms of nitrogen and within the water body it can exist as ammonia or, the more abundant, ammonium ion. While an essential nutrient to aquatic life, it can be harmful in excess. Excessive amounts of ammonia can lead to the death of aquatic macroorganisms (NCSU Water Quality Group, 1995). Because ammonia levels in zero-salinity surface waters increase with increasing pH and temperature levels, factors such as pH and temperature can affect ammonia toxicity to aquatic macroorganisms (EPA, 2013). Most natural surface waters are between a pH of 6.5 and 8.5. At a lower pH, the ammonium ion is produced, which is non-toxic to aquatic organisms, but at a pH above 9 unionized ammonia is predominate (EPA, 2013). Ammonia, much like many other pollutants, originates from nonpoint and point sources. Ammonia can be found in sewage treatment effluent. It has been shown to positively correlate with the proximity from treated effluent as well as the magnitude at the discharge points, i.e. levels of ammonia can increase if in closer proximity from treated effluent as well as higher magnitudes at the discharge point (Shin et al., 2013). Ammonia can also be found in agricultural fertilizers, ammonia-containing cleaning products, and industrial processes that release ammonia into the environment. It can be transported into the aquatic system via stormwater runoff, discharged from sewage treatment plants, and released through the deposition of airborne particles (NCSU Water Quality Group, 1995). The Ohio EPA Aquatic Life Ambient Water Quality Criteria for Ammonia recommends that ammonia levels not exceed 17 mg/L in a one-hour period and 1.9 mg/L in a 30-day period in streams/rivers to protect aquatic life (OH EPA, 2013).

Ammonia is a form of nitrogen obtained from a process in the nitrogen cycle. The four processes of the nitrogen cycle include nitrogen fixation, ammonification, nitrification, and denitrification. Nitrogen fixation converts gaseous nitrogen to ammonia; ammonification is the breakdown of organic matter such as amino acids to produce ammonia; nitrification oxidizes ammonia to nitrite and nitrate which is then taken up by plants; and denitrification reduces nitrates back to gaseous nitrogen. High nitrate content in drinking water can cause methemoglobinemia, commonly referred to as blue baby syndrome, which inhibits hemoglobin from transporting oxygen to the tissues. In surface water bodies, nitrogen can stimulate the growth of algae and other aquatic plants (eutrophication). This excessive growth of algae can result in unpleasant odors, interfere with recreational activities, decrease aesthetics, and can shade bottom-dwelling aquatic vegetation inhibiting their ability to photosynthesize and reducing productivity (NCSU Water Quality Group, 1995). Eutrophication can result in a decrease in oxygen levels in a water body when the algal blooms or other organic material die and decomposers consume large amounts of oxygen in the decomposition process. The decomposers deplete the oxygen to levels far below the normal range that is able to sustain aquatic life, creating an oxygen sag. Sources of nitrate include fertilizers, livestock excrement, and sewer overflows. Nitrogen is introduced as a pollutant into the aquatic system largely due to agricultural land use. Livestock production is a dominant factor for total nitrogen and ammonium loadings (Li et al., 2014). In addition, the percentages of cropland in watersheds can also significantly increase the nitrate loading in agricultural watersheds (Li et al., 2014).

Phosphorus, an essential nutrient, can exist in either organic or inorganic forms. Phosphorous can be transported in the runoff from urban sewage, agricultural fertilizer and manure, and urban/ residential animal waste as well as discharged into surface water bodies via sewage treatment plants. Once within the water body, phosphorus can be vbound to sediments on the bottom of lakes and reservoirs making phosphorus a growth limiting nutrient in most aquatic systems (Leone et al., 2008). In aquatic systems, available phosphorus is in a soluble or dissolved form known as orthophosphate. Phosphorus released from sediment is dependent on temperature, pH, redox conditions, biological activity as well as other chemical interactions. In an effort to control algal blooms, the EPA criterion for phosphorus states that phosphates should not exceed 0.1 mg/L if discharging into rivers or streams (EPA, 1988). Much like nitrogen and other nutrients, phosphorus can stimulate the growth of algae and other aquatic plants leading to eutrophication, dead zones, and hypoxia, as well as other similar effects including degradation and declination of the aesthetic surroundings, interfere with navigation, oxygen depletion, harmful algae blooms, and increased shading resulting in decreased productivity for benthic plant life (NCSU Water Quality Group, 1995). Harmful algal blooms produce dangerous toxins that can be directly toxic or stored within the tissues of small fish and shellfish (EPA, 2017). When these smaller organisms are eaten, these toxins can move up the food chain (or biomagnification) and affect larger organisms like turtles, dolphins, birds, and even humans. Land use can have a profound impact on the introduction of nutrients into the environment. High concentrations of nutrients, more specifically nitrogen and phosphorus compounds, occur primarily in agricultural and urbanized areas especially those with large animal operations, excessive fertilizing, or inadequately treated wastewater (Matysik et al., 2014).

Heavy Metals

As defined by the EPA, heavy metals are metallic elements with high atomic weights. Toxic heavy metals can harm living organisms at low concentrations and result in biomagnification. Heavy metal pollution results predominately from point sources such as mining, foundries and smelters, and other industrial processes (Tchounwou et al., 2014). Acid mine drainage from mining processes, and pesticides and herbicides containing trace amounts of heavy metals, are easily transferred into surface waters via runoff, (Hua et al., 2016). Despite having trace amounts of heavy metals in pesticides and herbicides, there is no correlation between heavy metals and nutrients (Skordas et al., 2015). Some heavy metals are toxic or carcinogenic (arsenic, lead, cadmium, mercury and chromium) to biotic organisms, and have been reported to affect cellular components such as the cell membrane, mitochondria, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair (Tchounwou et al., 2014). Some heavy metals are considered essential nutrients for plants and animals in lower concentrations. The macronutrients include zinc, copper, and chromium. While zinc and copper are not detrimental to human health at low levels, they can achieve devastating effects on aquatic life at very low concentrations (Brady, 1998). If water leaches through the mines, as copper and zinc are present in most mined ores, these pollutants can become present in toxic amounts in surface waters through runoff (Brady, 1998). Zinc, lead, and cadmium have been shown to be the most anthropogenically enriched metals due to mining activity (Hua et al., 2016).

Solids

Soil particles are introduced to surface water via stormwater runoff then deposited at the bottom of a water body. Sediment is one of the most common pollutants in surface waters. Many processes can contribute to an increase in sediment, but the most concentrated sediment releases come from construction activities, releasing ten times more than any other land use (Line et al., 2002). Two types of solids that are of concern regarding water quality: total suspended solids and total dissolved solids. Total suspended solids (TSS) are solids that can be trapped by a filter. TSS can decrease water visibility and prevent sunlight from reaching benthic vegetation, reducing photosynthesis. As photosynthesis is reduced, oxygen levels are depleted. Low dissolved oxygen levels can result in the death of aquatic macroorganisms. TSS can also increase water temperature resulting in further depletion of dissolved oxygen and a higher risk of aquatic degradation (Murphy, 2007). Additions of TSS can often result in an increase of bacteria, nutrients, and metals in the water since many contaminants can attach to and persist in the sediment (Chudoba et al., 2013). TSS can also be impacted by land use such as urban runoff and erosion, however, total suspended solids were not shown to be correlated with the percentage of impervious surface (Line, 2013). Total dissolved solids (TDS) are those that can pass through a filter. Total solids encompass both total suspended solids and total dissolved solids. The effects of TDS are similar to those of TSS. If concentrations are too high or too low, the growth of aquatic macroorganisms can be affected and death could occur, (Murphy, 2007).

Dissolved Oxygen

Dissolved oxygen (DO) is the amount of oxygen dissolved in the water, which is needed by aquatic organisms to survive. DO can be influenced by several factors including season, time of day, temperature, and salinity (EPA, 2006). Dissolved oxygen levels can fluctuate seasonally due to the relationship between saturation and temperature. During summer months, when temperatures are higher, saturation is lower because warm water holds less oxygen than cold water. The reverse is true for lower temperatures during winter months. As water gets colder, more dissolved oxygen can be held because the water is not saturated as easily. Dissolved oxygen is closely monitored by wastewater treatment plants and in surface waters (Clesceri et al., 1999). During times of excess decomposition of organic material by microorganisms, DO levels can become low, which is called hypoxia, or become completely devoid of oxygen, which is referred to as anoxic (EPA, 2016). If oxygen levels become too low, aquatic life can begin to die. Excess decomposition can be brought on by eutrophication caused by high levels of nutrients in a water body. Biochemical oxygen demand (BOD) is a measure of the amount of oxygen consumed by microorganisms as they break down organic matter. The higher the BOD content, i.e. the more oxygen consumed, the faster oxygen is depleted in the water body. Runoff from urban settings can carry pet wastes and other organic material from impervious surfaces, and residential lawns, which can increase the BOD five to ten times as compared to nearby areas (Arienzo et al., 2000). Dissolved oxygen can also be released in wastewater effluent. Dissolved oxygen is positively correlated with the distance from treated effluent and its magnitude at the discharge point (Shin et al., 2013).

Sources of Pollution

Water pollution can be influenced by several factors, which have been briefly mentioned previously. Weather, namely rainfall, is a large factor that plays into water quality. In general, fecal bacteria levels are correlated with rainfall (Staley et al., 2013) meaning bacterial densities during periods of wet weather are statistically significantly higher than bacterial densities during periods of dry weather (Gannon and Busse, 1989). Storms that exhibit high fecal coliform concentrations tend to be those that were preceded by relatively dry conditions and included high rainfall intensity (Sullivan, 2004). Moreover, fecal and total coliform concentrations are lower in the summer as opposed to the winter during dry weather flows (Ashley and Dabrowski, 1995). During periods of drought, fecal coliforms from wild animals dominate riparian zones (Shehane et al. 2005). Precipitation runoff can give mobility to pollutants and introduce bacteria into the water system causing contamination. During lengthy dry periods, animal feces can accumulate on embankments. During a heavy rainfall, this accumulated excrement is washed into the nearby surface waters intensifying fecal coliform numbers. Fecal coliform and *E. coli* concentrations can be highly variable, especially along urban streams, however, they typically increase with streamflow and precipitation events (Sanders et al., 2013).

Stormwater is typically associated with runoff water, which is why pollutant concentrations are often higher in wet conditions as opposed to dry conditions. During precipitation events, stormwater runoff contributes largely to water pollution. As runoff flows across impervious surfaces, it picks up any contaminants in its wake, which includes nutrients, fecal material, organic material, chemicals, and other pollutants. These contaminants can either flow directly into surface waters or into a sewer grate where it is sent to the wastewater treatment plant. Individual sources of stormwater can differ in nutrient concentrations as well as fecal bacterial concentrations (Reifel et al., 2009). The highest bacterial concentrations occur during the early phases of stormwater runoff with peak concentrations normally preceding peak flow, which is the maximum instantaneous discharge of a river at a given location (Tiefenthaler et al., 2011). These bacterial concentrations remain higher in wet conditions for 48 hours after peak flow than in dry conditions (Stoeckel and Covert, 2002). Contaminant standards are often exceeded in waters containing greater than 10% stormwater (Reifel et al., 2009).

Land use refers to the modification of the natural environment into built environment and can considerably impact its surroundings. Land use can be classified into many different categories which include developed/urban, impervious surface, forested, agricultural, wetland, and many others. Pollutants can be correlated to specific land uses. Total coliform inputs into rivers are related to animal agricultural activity directly or to ineffective treatment of human waste from residences in agricultural areas (Twiss et al., 2006). Differences in nutrient levels reflect differences in land use (Williams et al., 2012). Nitrogen inputs are prevalent from construction, residential, and golf course land uses, while total phosphorus inputs are reflected in golf courses, pastures, and residential land uses in those orders (Line et al., 2002). Elevated levels of nitrogen can be found in land uses related to forest management while greater ammonia levels are found in land uses related to agricultural functions (Amarathunga and Kazama, 2016). Total nitrogen and ammonia concentrations are also positively associated with urban areas although nitrogen, total phosphorus, and total suspended solids are not correlated to the percentage of impervious surface (Ding et al., 2015; Line, 2013). Combined sewer overflows (CSOs) are included as land uses. Instead of having separate pipes for both stormwater and municipal waters, combined sewer overflows combine the waters, which flow to the wastewater treatment plant. However, in times of heavy rainfall, combined sewers can overflow discharging untreated waste into receiving surface waters. *E. coli* concentrations can be linked to CSO discharges caused by precipitation exceeding 10mm or spring snowmelt (Madoux-Humery et al., 2015). Moreover, locations closer to areas with high densities of active septic tanks or more urbanized land uses tend to have higher fecal coliform densities (Kelsey et al., 2004).

Macroinvertebrates

Pollutant levels are not the only indicators of water quality. Aquatic macroinvertebrates are also identifiers of good or poor water quality. The Biotic Index classifies aquatic insect taxa according to pollution tolerance: Class I: Pollution Sensitive Taxa, Class II: Moderately Tolerant Taxa, and Class III: Pollution Tolerant Taxa (Sharpe et al., 1975). Many aquatic insect species are not tolerant of pollution. The presence of many pollution tolerant taxa such as true flies, flatworms, and aquatic earthworms indicate predominately poor water quality. Three orders of aquatic macroinvertebrates are commonly used as an indicator of good water quality due to their pollution sensitive nature. These orders include Ephemeroptera: mayflies, Plecoptera: stoneflies, and Trichoptera: caddisflies. As a whole, these three orders are referred to as the EPT Index and are used to monitor water quality. The EPT Index is based on the premise that higher quality streams/rivers have a greater species richness, i.e. greater number of different species present. As pollution levels increase, a lower species richness is expected for the stream (Watershed Science Institute, 2012).

Mill Creek Watershed

The watershed study area (Figure 1) spans from Youngstown, OH to Columbiana, OH. Mill Creek is the main river is roughly 39 kilometers in length starting in Columbiana, OH and ends in Youngstown, OH where it flows into the Mahoning River. Mill Creek contains several smaller tributaries that flow into the main river as well as small ponds, lake, wetlands and the three man-made lakes in Mill Creek MetroPark. The land comprising the watershed is relatively flat with steeper slopes and lower elevations around the main river and tributaries (Figures 2 and 3). Mill Creek MetroParks located on the northern end near the Mahoning River, has been experiencing higher levels of water contamination in recent years, threatening recreational activities. Analysis of watershed parameters can provide data to Mill Creek MetroParks and the Mahoning County District Board of Health to help identify potential contamination sources within the park.

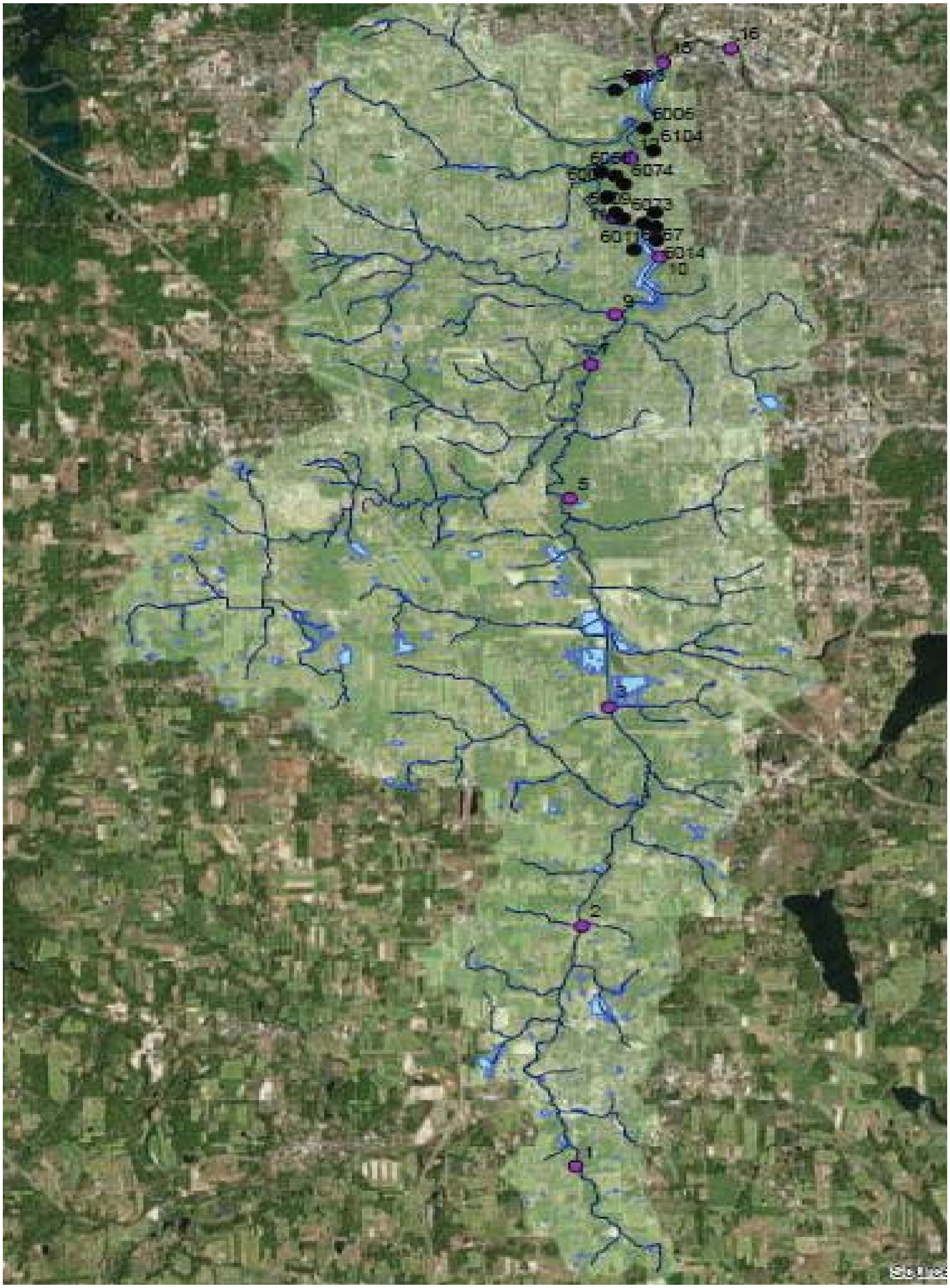

Figure 1 Mill Creek Watershed located in the southern part of Mahoning River Watershed in northeast Ohio. Purple markers indicate selected sample sites and black markers indicate combined sewer overflows (CSOs) that deposit into Mill Creek.

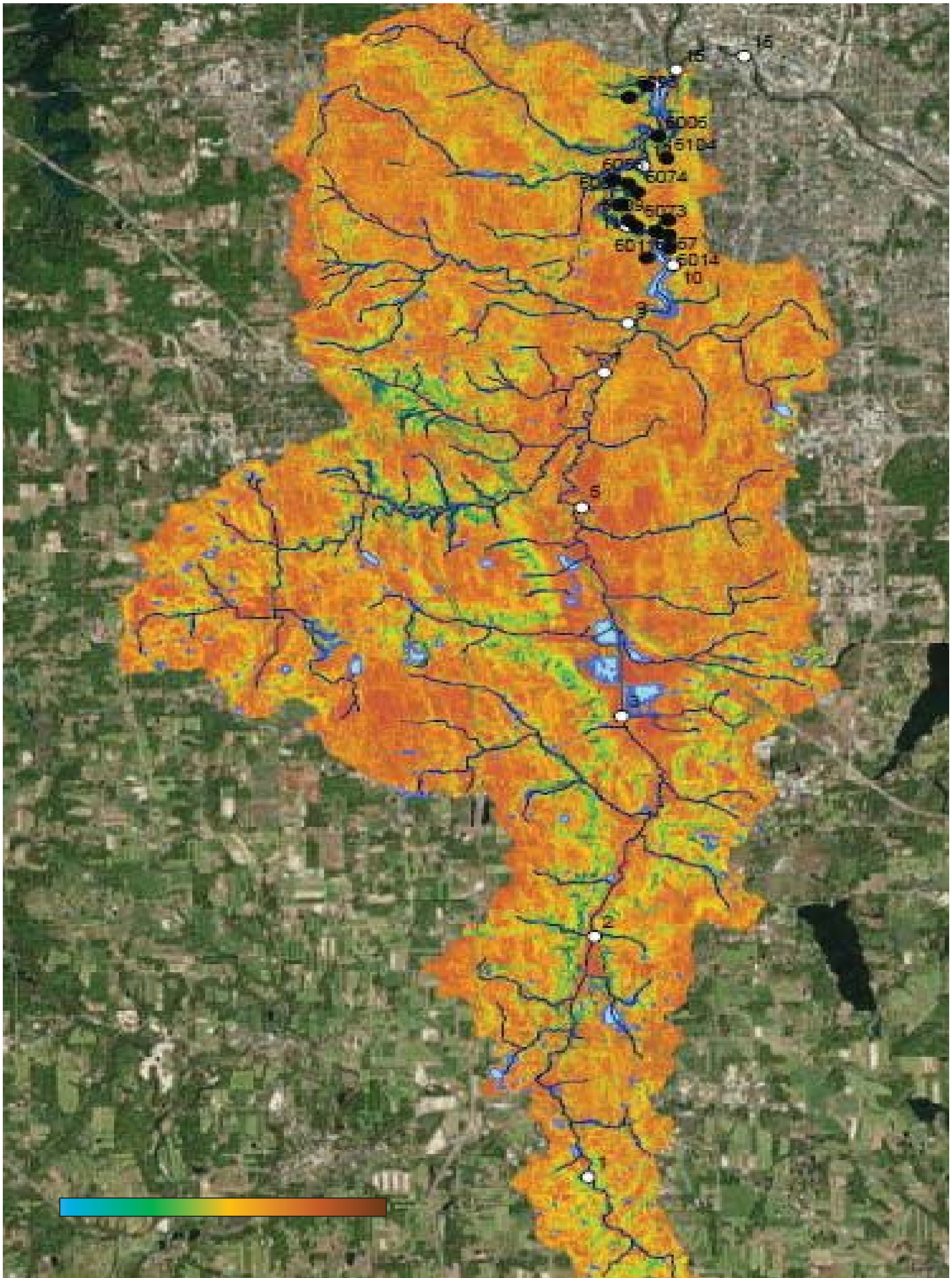

Figure 2 Mill Creek Watershed slope gradient. Brown areas indicate flatter land and blue/green areas indicate steeper slopes. White markers indicate selected sample sites and black markers indicate combined sewer overflows (CSOs) that deposit into Mill Creek.

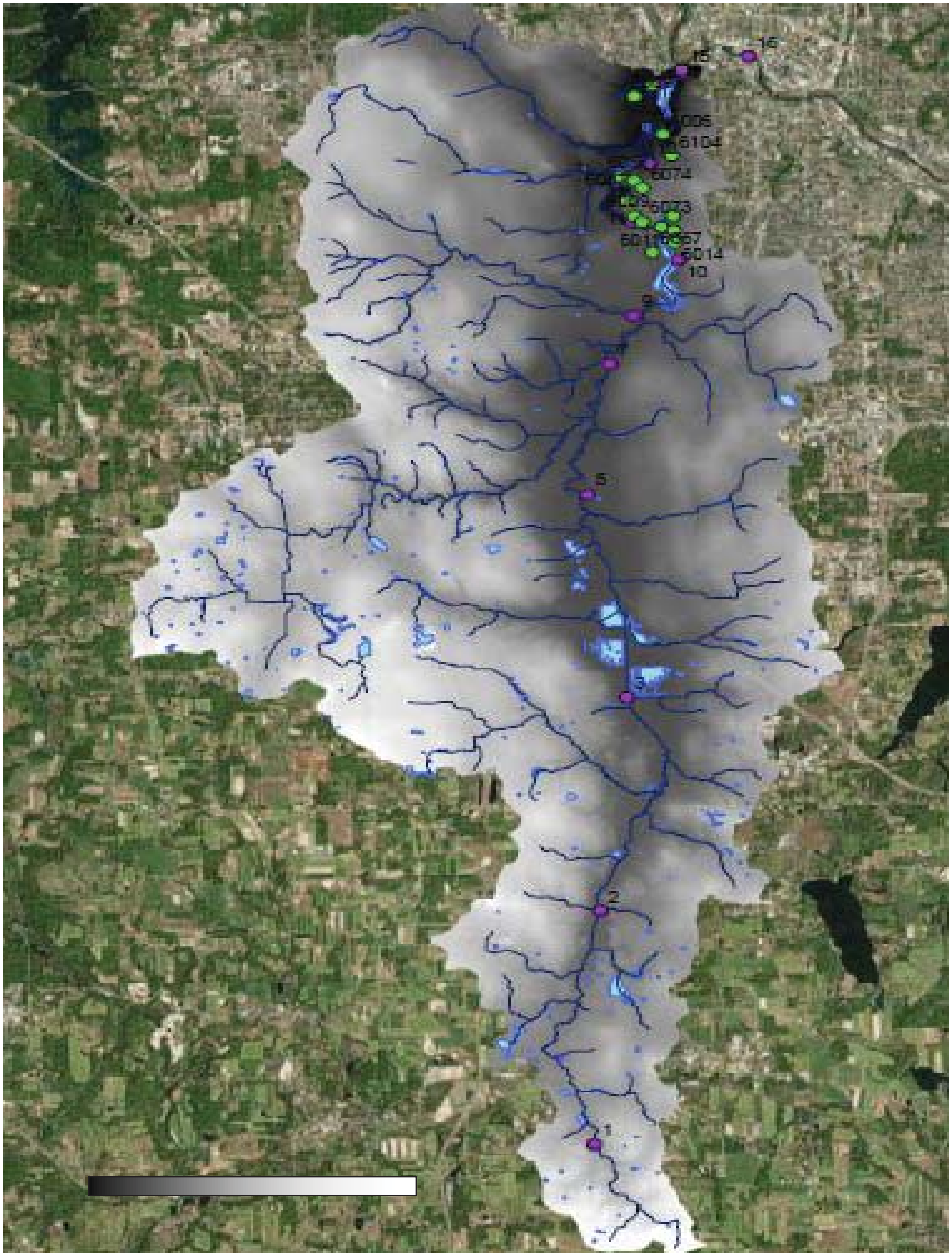

Figure 3 Mill Creek Watershed digital elevation model (DEM). Darker areas indicate lower elevations and lighter areas indicate higher elevations. Purple markers indicate selected sample sites and green markers indicate combined sewer overflows (CSOs) that deposit into Mill Creek.

Hypothesis

Rain events negatively affect water quality in areas of intense anthropogenic land use. Areas of agricultural land use, which includes farming and livestock, will result in more nutrients, fecal coliforms, and solids due to livestock waste runoff, fertilizer use, and erosion. Areas of industrial and urban land use will produce more fecal coliforms and metals due to residential animal waste runoff and industrial processes.

Objectives

The objective of this study was to evaluate the land use and associated surface water quality in Mill Creek and to establish associated sampling sites. Sampling was done during low flow or baseline conditions and 24-48 hours after significant rainfall events (>2.5cm). Onsite analysis included temperature, flow, dissolved oxygen, pH, and conductivity. Laboratory testing for additional water quality parameters included coliforms (total and fecal), biochemical oxygen demand, metals, orthophosphates, ammonia, and solids (total, suspended, dissolved and volatile).

Chapter 3 Materials and Methods

Study Area

The Mill Creek watershed spans from Youngstown, OH in Mahoning County to Columbiana, OH in Columbiana County and is comprised of multiple land uses including residential, agricultural, golf courses, and impervious surfaces (Figure 4). The northern half of Mill Creek's watershed land use is characterized by densely populated urban and suburban areas mainly predominated by residential and commercial land use while the southern half of the watershed is much more rural and devoted to agriculture (McCracken, 2007). Agricultural land use accounts for 5.2% of the northern sub-watershed (Figure 5), 40% of the mid-western sub-watershed (Figure 6), and 51.9% of southern sub-watershed (Figure 7) (McCracken, 2007). Impervious surfaces make up approximately 15.9% of the northern sub-watershed, 5.5% of the mid-western sub-watershed, and 6.5% of the southernmost sub-watershed (McCracken, 2007). Mill Creek flows north from Fairfield Township in Columbiana County to Youngstown in Mahoning County making its way through several lakes including Lake Glacier, Lake Newport, and Lake Cohasset on the north end of the creek, eventually flowing to the Mahoning River. The river has several small tributaries, such as Turkey Run, Indian Run, Anderson Run, Cranberry Run and several others.

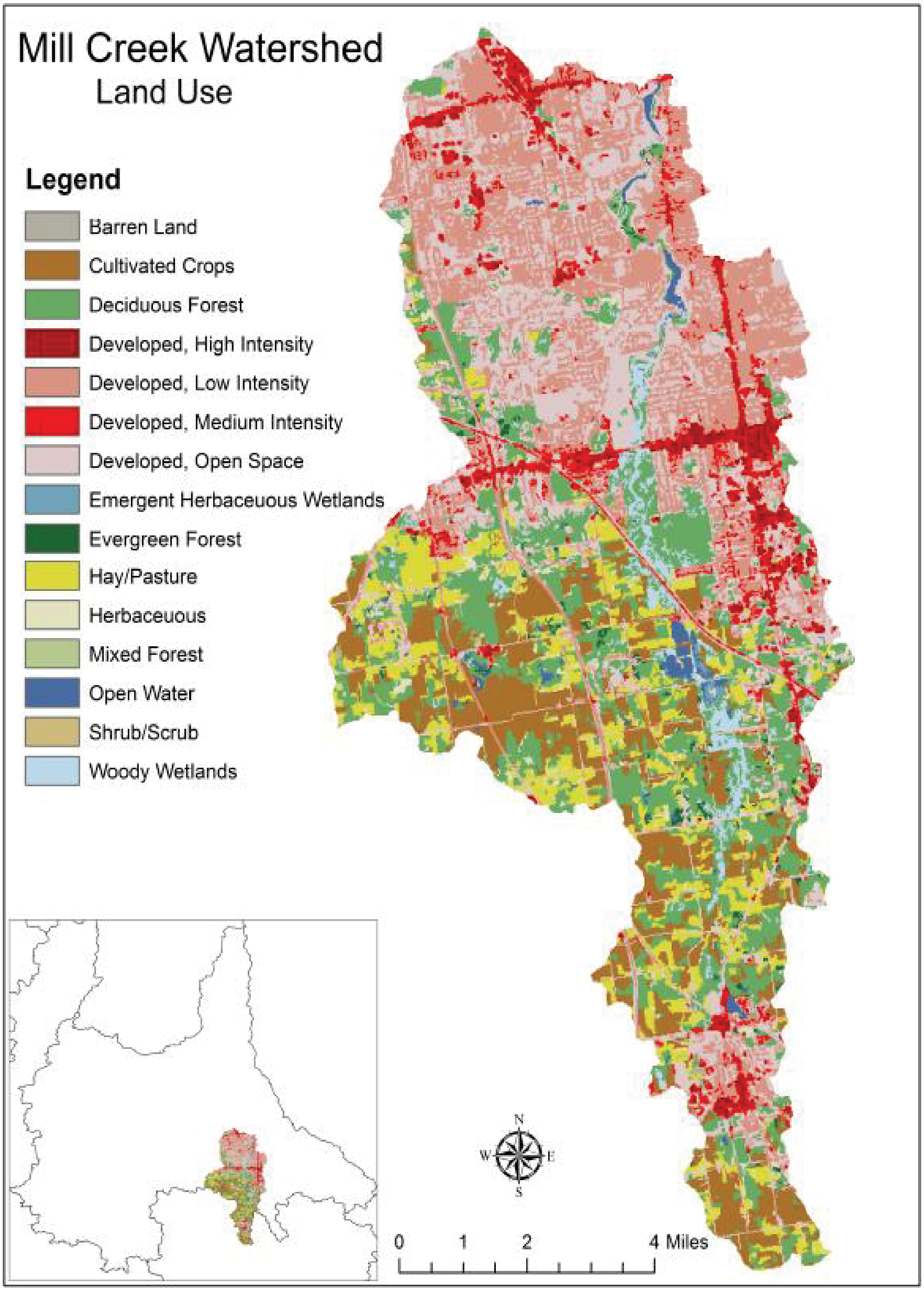

Figure 4 Mill Creek Watershed land use (Kimosop, 2017)

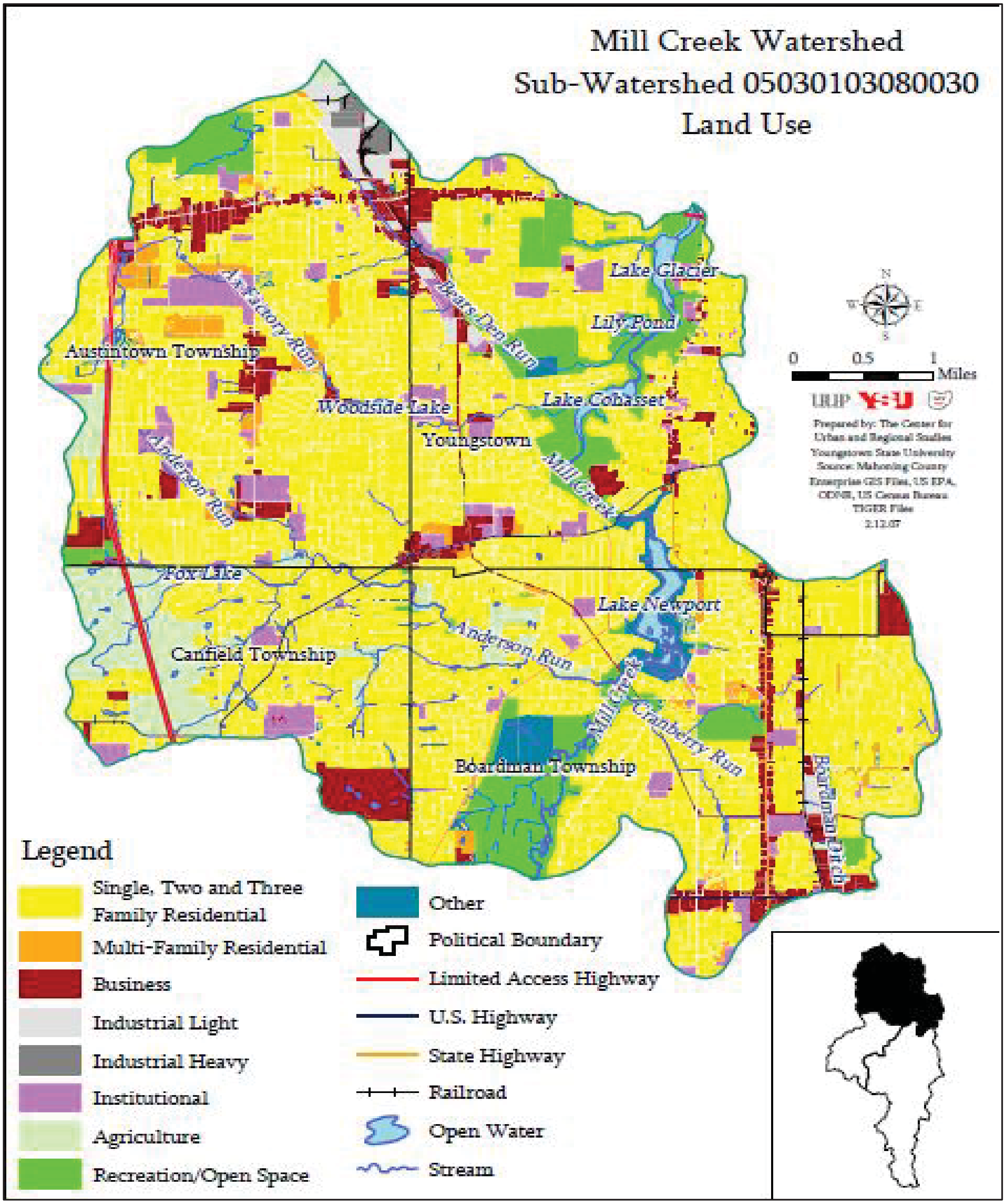

Figure 5 Mill Creek's northern sub-watershed land use (McCracken, 2007)

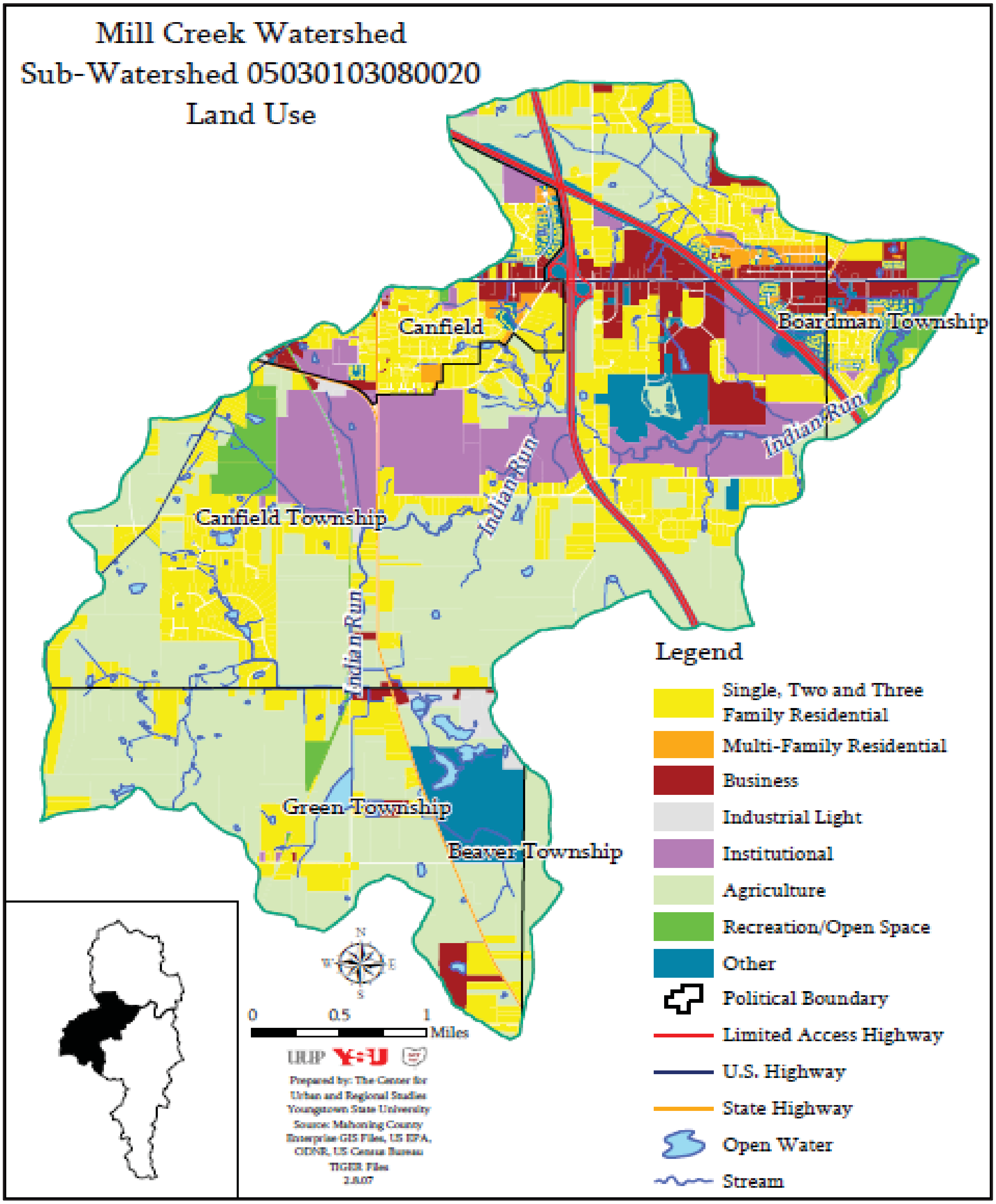

Figure 6 Mill Creek's mid-western sub-watershed land use (McCracken, 2007)

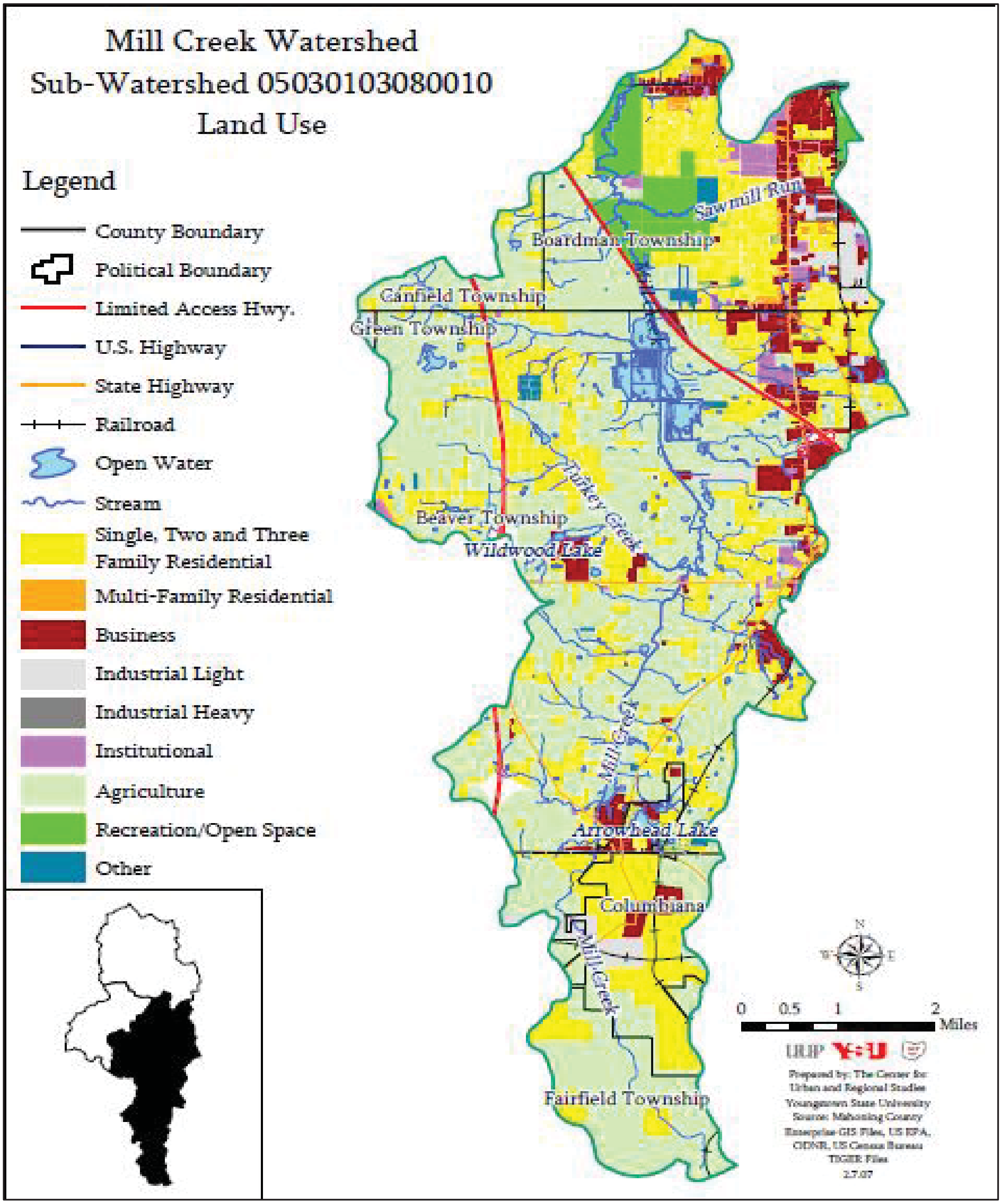

Figure 7 Mill Creek's southern sub-watershed land use (McCracken, 2007)

Site Characteristics

Sixteen sample points of interest (Figure 8) were plotted along the main river in Mill Creek's watershed. Due to poor accessibility and safety concerns four sample points were removed leaving the final 12 sites (Tables 1 through Table 13).

Table 1 Site Land Use Characteristics

Site 1	Downstream row crop farm, roadways
Site 2	Cattle farm, roadways
Site 3	Adjacent row crop farm
Site 5	Boardman WWTP, two large housing developments on either side of site
Site 7	Golf course, housing development, bike trail
Site 9	Roadways, housing developments, Newport wetlands
Site 10	Newport Lake, urban park with wildlife, largely residential area
Site 11	Roadways, urban park with wildlife, largely residential area
Site 12	Lake Cohasset, urban park with wildlife, largely residential area
Site 14	Lake Glacier, urban park with wildlife, roadways, largely residential area
Site 15	Roadways, interstate 680, largely residential, many industries
Site 16	Largely urban area with many industries

Additional Site Information

Table 2 Site 1, Intersection of Metz Rd. and Camelot Dr.

Elevation	335 m
Surrounding Land Use	Agriculture, impervious surfaces (intersection)
Approximate Depth	0.3 m
General Speed of Flow	Slow
Shading	Semi-shaded
Sampling Location	Sampled on right side of overpass
County	Columbiana
Approximate Width	2 m
Additional Information	Downhill from large agricultural farm

Table 3 New Site 2, Near farm on Renkenberger Rd. Site 2 was changed to "New Site 2" location after the May and June sampling, therefore, there is a lack in data for site 2 during those months.

Elevation	321 m
Surrounding Land Use	Agriculture, impervious surfaces
Approximate Depth	1 m
General Speed of Flow	Slow
Shading	No shade
Sampling Location	Sampled from ~2 m above stream
County	Columbiana
Approximate Width	2 m
Additional Information	Next to large cattle farm

Table 4 Site 3, Intersection of Lynn and Bassinger

Elevation	299 m
Surrounding Land Use	Agriculture on west, wetland on the east, some, impervious surfaces
Approximate Depth	1 m
General Speed of Flow	Slow
Shading	Shaded
Sampling Location	Sampled next to tree that overhangs stream
County	Columbiana
Approximate Width	5-6 m
Additional Information	Sampled approximately 23 m down from roadside

Table 5 Site 5, Boardman WWTP

Elevation	348 m
Surrounding Land Use	Industry (wastewater treatment plant), residential, Mill Creek Preserve
Approximate Depth	1 m at sample spot
General Speed of Flow	Fast
Shading	Semi-shaded
Sampling Location	Sampled ~300ft down from treatment plant
County	Mahoning
Approximate Width	5 m
Additional Information	Treatment plant deposits into stream

Table 6 Site 7, End of Lundy Lane (across bike path)

Elevation	364 m
Surrounding Land Use	Impervious surfaces, residential
Approximate Depth	0.3 m at sample spot
General Speed of Flow	Slow
Shading	Semi-shaded
Sampling Location	Downhill from bike path
County	Mahoning
Approximate Width	3 m
Additional Information	Crossed bike path from parking spot and sampled at the bottom of the bike path

Table 7 Site 9, Mill Creek near Cranberry Run at Shields Road overpass

Elevation	300 m
Surrounding Land Use	Impervious surfaces
Approximate Depth	1 m
General Speed of Flow	Slow
Shading	Shaded
Sampling Location	Cranberry Run 15 m. from Shields Rd , 3 m from bridge
County	Mahoning
Approximate Width	2 m
Additional Information	Jumped down to small ledge 2 m lower in elevation from trail and sampled from there

Table 8 Site 10, Lake Newport (off boat launch dock)

Elevation	300 m
Surrounding Land Use	Impervious surfaces
Approximate Depth	2 m at sample spot
General Speed of Flow	None
Shading	No shade
Sampling Location	Off Newport lake boat launch dock
County	Mahoning
Approximate Width	N/A
Additional Information	Large amounts of duckweed on top of water

Table 9 Site 11, Lanterman's Mill, Trail 10

Elevation	320 m
Surrounding Land Use	Impervious surfaces
Approximate Depth	1 m at sample spot
General Speed of Flow	Fast
Shading	Semi-shaded
Sampling Location	Rocky clearing off trail 10
County	Mahoning
Approximate Width	6-9 m
Additional Information	Walked ~402-805 m miles to sample site

Table 10 Site 12, Lake Cohasset, Trail 5

Elevation	320 m
Surrounding Land Use	Impervious surfaces
Approximate Depth	1 m at sample spot
General Speed of Flow	None
Shading	No shade
Sampling Location	Wooded area near fallen tree
County	Mahoning
Width	N/A
Additional Information	Walked ~402-805 m miles to sample site

Table 11 Site 14, Lake Glacier (off paddle boat dock)

Elevation	312 m
Surrounding Land Use	Impervious surfaces
Approximate Depth	2 m deep at sample spot
General Speed of Flow	None
Shading	No shade
Sampling Location	Off paddleboat dock approx. 31 m from road
County	Mahoning
Width	N/A
Additional Information	Goose feces covered most of the lawn and dock during summer

Table 12 Site 15, Mill Creek to Mahoning River (under overpass)

Elevation	285 m
Surrounding Land Use	Industry, impervious surfaces, residential
Approximate Depth	1 m at sample spot
General Speed of Flow	Slow
Shading	Shaded under overpass
Sampling Location	Underneath overpass approx. 15 m from road
County	Mahoning
Approximate Width	24-31 m
Additional Information	Where Mill Creek meets Mahoning

Table 13 Site 16, Mahoning River at B&O Station (off dock)

Elevation	285 m
Surrounding Land Use	Impervious surfaces, industry, residential
Approximate Depth	2 m at sample spot
General Speed of Flow	Fast
Shading	No shade
Sampling Location	Off dock downhill from B&O Banquet Center
County	Mahoning
Approximate Width	9-12 m
Additional Information	Historically poor water quality for Mahoning River

Baseline and event measurements were taken no more than twice a month at each site from May 2016 to November 2016. Baseline measurements were taken during periods of little to no rainfall, whereas event measurements were taken no earlier than 24 hours after a significant precipitation event. Significant precipitation events were outlined as rain events with at least 2.5cm (one inch) of cumulative rainfall. Field data gathered included temperature, stream flow, pH, electrical conductivity, dissolved oxygen, and depth. Weather conditions were also recorded during each sampling. Twelve 1000mL Nalgene bottles were used for duplicate sampling from each site. At each site, bottles were rinsed twice with sample water, then held until full and capped underwater to ensure the least amount of air possible within the sample. Field parameters were taken using a YSI

Professional Plus Multiparameter Meter and a Flowatch meter. Samples were stored in a cooler until transported back to the University for laboratory analysis. Laboratory data produced consisted of fecal and total coliform counts, biochemical oxygen demand (BOD), soluble and total solids, soluble orthophosphate, ammonium, anions, and metals. Laboratory parameters were analyzed within Youngstown State University's environmental science laboratories using methods from *Standard Methods for the Examination of Water and Wastewater* and *Methods of Soil Analysis: Part 3—Chemical Methods* to conduct each test. Coliforms and BOD_5 were analyzed within 24 hours of collection of samples (Clesceri et al., 1999).

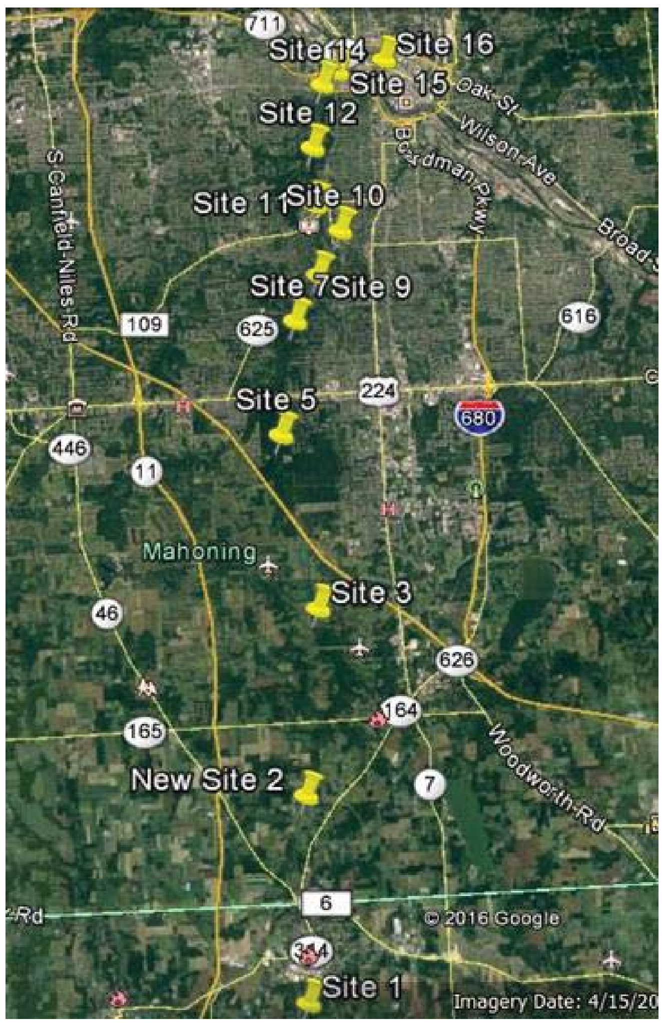

Figure 8 Mill Creek sample sites plotted on Google maps

BOD_5: 5-Day BOD Test

Dilution water was prepared by adding deionized water to a desired volume then adding 1mL of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ per each liter of water as described in *Standard Methods for the Examination of Water and Wastewater* (Clesceri et al., 1999). Seed was obtained from the Youngstown Wastewater Treatment Plant. Each sample site had a minimum of three repetitions with various volumes of sample water (e.g. 50, 100, and 200mL) to ensure valid results. Each sample received 3mL of seed and was filled to volume (300mL) with dilution water. Quality assurance methods included two water blanks, two seeded blanks, and two glucose-glutamic acid (GGA) standards. Dissolved oxygen of each sample was measured using a YSI 5000 Series Dissolved Oxygen Meter (Model 5010), sealed (water sealed and parafilm), and placed in the incubator at 20°C. After a 5-day incubation period, the BOD bottles were removed from the incubator and dissolved oxygen was measured and recorded again (Clesceri et al, 1999).

Total Coliforms: Standard Total Coliform Membrane Filter Procedure

Four sample volumes: 1, 5, 10, and 50mL were used as suggested sample volumes in accordance with Table 9222:I (Clesceri et al., 1999). Using sterile forceps, a sterile membrane filter was placed, grid side up, over a porous plate of receptacle. The funnel was placed over the plate and locked into place. Ten milliliters of sterilized deionized water was used to rinse the filter paper and then vacuumed out. The specified amount of sample water was then added to the filter and vacuumed out. For volumes less than 10mL, 10mL of deionized water was added to the sample for dispersion purposes before vacuuming out. Once vacuumed, the funnel was rinsed for 30 seconds (~30 mL) with deionized water. The membrane filter was removed with sterile forceps and placed directly on a dish of mEndo agar-based medium. Blanks were run with 50 mL of sterilized deionized water to insure no contamination was in the water source or equipment. Dishes were inverted, and incubated at 35°C for 22-24 hours. Colonies were counted after incubation (Clesceri et al., 1999).

Fecal Coliforms: Fecal Coliform Membrane Filter Procedure

Four sample volumes: 1, 5, 10, and 50mL were used as suggested sample volumes in accordance with Table 9222:I. Using sterile forceps, a sterile membrane filter was placed, grid side up, over a porous plate of receptacle. The funnel was placed over the plate and locked into place. Ten milliliters of sterilized deionized water was used to rinse the filter paper and then vacuumed out. The specified amount of sample water was then added to the filter and vacuumed out. For volumes less than 10mL, 10mL of deionized water was added to the sample for dispersion purposes before vacuuming out. Once vacuumed, the funnel was rinsed for 30 seconds (~30 mL) with deionized water. After rinsing, the funnel was removed. The membrane filter was removed with sterile forceps and placed directly on a dish of mFC agar-based medium. Blanks were run with 50 mL of sterilized deionized water to insure no contamination was in the water source or equipment. Dishes were inverted, and incubated at 44.5°C for 22-26 hours. Colonies were counted after incubation (Clesceri et al., 1999)

Solids: Total Suspended Solids Dried at 103-105°C

A pre-weighed glass fiber filter disk was placed on a filtration apparatus. Volumes between 50 and 100mL of unfiltered sample were run through each filter. The vacuum was applied, and the disk was washed with 20mL of deionized water. Once all water had been removed, weighing dishes were taken to the oven to be dried at 103-105°C. Filters were weighed again the following day (Clesceri et al., 1999)

Solids: Total Solids Dried at 103-105°C

Volumes of 25 and 50mL of unfiltered sample were added to previously weighed crucibles and placed in the oven to be dried at 103-105°C. Crucibles were weighed again the following day (Clesceri et al., 1999).

Solids: Fixed and Volatile Solids Ignited at 550°C

Residue produced from soluble and total solids samples were ignited in a furnace at a temperature of 550°C for 15-20 minutes. After allotted time, samples were placed in the desiccator and brought to room temperature. Once cooled, filter disks or crucibles were weighed again on the balance (Clesceri et al., 1999).

Soluble Reactive Phosphate (Orthophosphate): Ascorbic Acid Method

Five normal (5N) sulfuric acid, potassium antimonyl tartrate solution, ammonium molybdate solution, and 0.1M ascorbic acid were used to make a combined reagent (Clesceri et al., 1999). Twenty-five milliliters of each filtered sample was added to a clean 125mL Erlenmeyer flask. Four milliliters of the combined reagent was added to each sample and mixed thoroughly. Two repetitions were used for each sample. After at least 10 minutes, but no more than 30 minutes, absorbance was measured on the Genesys 10S VIS spectrophotometer at 880nm. A calibration curve was prepared using eight standards at the following concentrations: 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.50, and 1.00 mg/L and used to calculate amount of orthophosphate in each sample (Clesceri et al., 1999).

Ammonia: Colorimetric Method

Sodium salicylate-sodium nitroprusside, buffered hypochlorite regent, and ethylene diaminetetraacetic acid (EDTA) were used as reagents. Twelve and a half milliliters of filtered sample water was added to a 25mL volumetric flask. One mL of EDTA was added and contents were mixed. Next, 4mL of sodium salicylate-sodium nitroprusside was added, mixed, and deionized water was used to bring the volume up to approximately 20mL. Lastly, 2mL of the hypochlorite buffer was added, and deionized water was used immediately to bring the volume up to 25mL. Two repetitions were used for each sample. The contents of the flasks were thoroughly mixed and placed in a water bath set at 37°C for 30 minutes. After 30 minutes, the flasks were removed from the water bath and allowed to cool to room temperature. Once cool, absorbance was measured on the Genesys 10S VIS spectrophotometer at 667nm. A calibration curve was prepared using 6 standards: 0,1,2,3, 5, and 10ppm and used to calculate mg/L of ammonium in each sample (Sparks, 1996).

Chapter 4 Results and Discussion

Sampling was conducted during the period of May 25, 2016 to November 4, 2016. Results are separated according to parameter and month sampled. Field parameters recorded were pH, dissolved oxygen, temperature, and conductivity. Over the course of this project, seven samples were taken from the 12 sites, three of which were baselines and four were rain events. For rain events, samples were taken 24- 48 hours after a significant rainfall. Significant rainfall was defined as times where precipitation was greater than 2.5cm in a 24 to 48-hour period. The amount of precipitation recorded for the four events sampled were August 1: 3.12cm, September 2: 3.86cm, October 1: 4.06cm, and October 21: 10.13cm. Site 5 for October 1 had no data due to the site was accessed through the Boardman Wastewater Treatment Plant which was closed on that date. Baselines, May 25, June 16, and November 4, were taken during relatively dry periods with very little to no rainfall.

Statistical analyses, Spearman correlation and Analysis of Variance (ANOVA), were performed on each parameter using the program SPSS (version 22.0; IBM, 2013). Sig (2-tailed) represents the p-value of each analyte. An alpha value of 0.05 was used for both Spearman correlation and ANOVA. A value of 1.000 on a Spearman's correlation indicates a perfect positive correlation while a value of -1.000 indicates a perfect negative correlation. A p-value less than 0.05 shows statistical significance, whereas a p-value greater than 0.05 indicates no statistical significance. ANOVA is used to test differences between two or more means.

On Site Analysis

Water temperatures over the 7-month period ranged from a maximum of 26.9°C at site 5 in August, to a minimum of 10.1°C at site 7 in November (Figure 9). Temperature trends were as expected with higher surface water temperatures predominating in the summer months and declining into the fall months.

The pH values ranged from a high of 8.53 on May 25 at site 14 to a low of 6.15 on October 1 at site 9 (Figure 10). These pH values are within normal pH range of 6.5-8.5 for surface water (ODH, 2014). Site 9 on October 1 was the only recoding where pH was slightly outside the normal range at 6.15, which could indicate the introduction of an acidic substance upstream of site 9. Site 9 is near Anderson Creek and Shields Road; the runoff could have brought lower pH material into the creek. However, pH increased again downstream at the next sampling site during the same sampling date (October 1, Figure 10). This trend is not recurring with the other months.

Conductivity ranged from 1190.0 µS/cm to 215.9 µS/cm (Figure 11). Conductivity is a measure of electrical current flow through a solution. A higher conductivity value indicates a greater amount of dissolved salts and inorganic chemicals in the water, which can harm organisms that are not adapted to conductivity values outside of a specific range. Average conductivity of streams can range anywhere from 50 to 1500 µS/cm with higher conductivity values (e.g.> 2000 µS/cm) can decrease aquatic organism diversity. All observed values are within the acceptable range for warm water habitat indicating no excess salts are being introduced to the creek.

Dissolved oxygen values ranged from 3.48 mg/L to 10.14 mg/L (Figure 12). Relatively low values of DO, such as 2 mg/L and under, will not support desirable aquatic life. Dissolved oxygen levels at 5 mg/L and above is an acceptable level of dissolved oxygen that will support many types of aquatic life (OH EPA, 2017). For many sites, DO values are lower than 5 mg/L. Values are much lower from May to September when temperatures are warmer as opposed to October and November as temperatures decline Figure 9). Most probable cause is temperature and water turbulence. As temperatures increase during warmer months, the maximum dissolved oxygen holding capacity decreases. The contrary is expected during winter months where temperatures are colder. Areas with riffles will also have higher amounts of dissolved oxygen. In summation, it is expected for dissolved oxygen to be lower during warmer seasons in calm water and higher in colder seasons with more turbulent water (Figure 13).

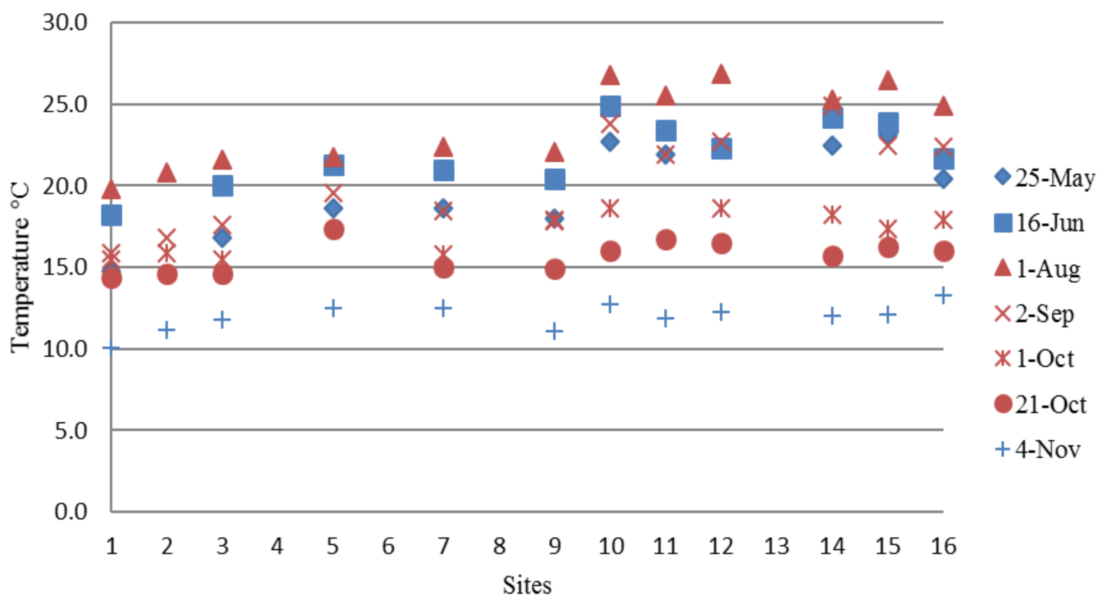

Figure 9 Surface water temperature at sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

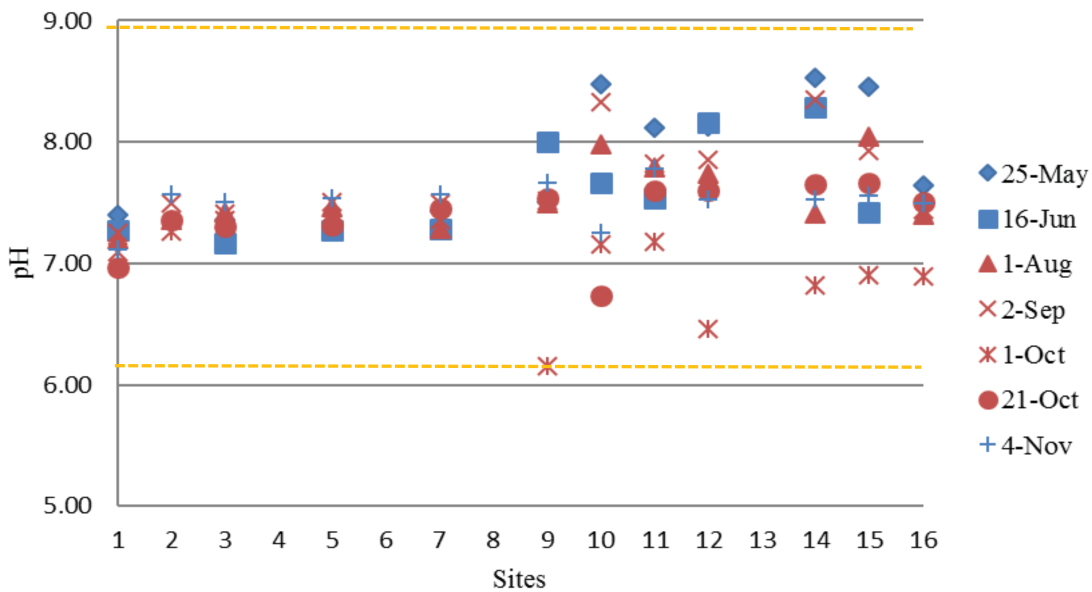

Figure 10 Mill Creek surface water pH at sample sites in Mill Creek, 2016. All pH stay within expected range for surface water except for Site 9 on October 1, which was the lowest pH of 6.1. pH returns to normal ranges at the following sample site. Blue markers indicate baseline values and red markers indicate rain events.

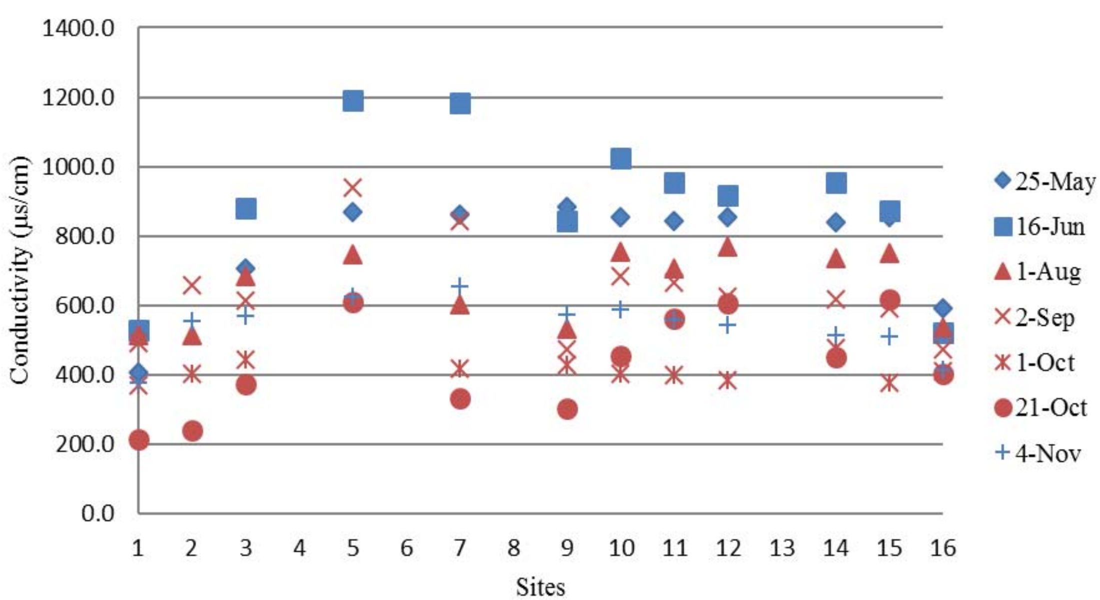

Figure 11 Conductivity in surface water from site in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

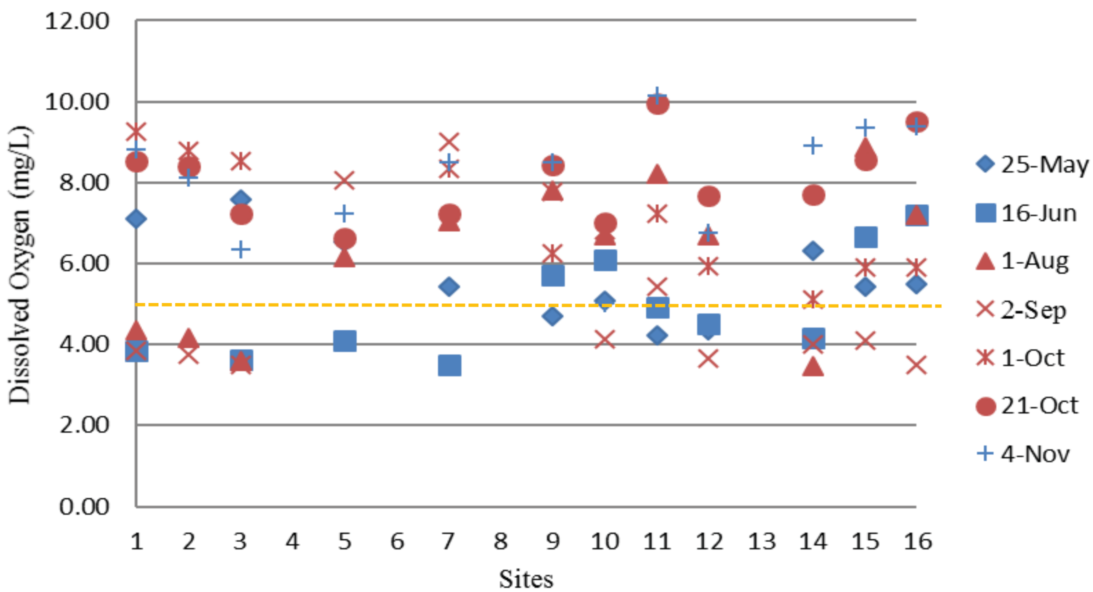

Figure 12 Dissolved oxygen in surface water from site in Mill Creek, 2016. Dashed yellow line indicates the level of dissolved oxygen (5 mg/L) required to sustain aquatic life. Blue markers indicate baseline values and red markers indicate rain events.

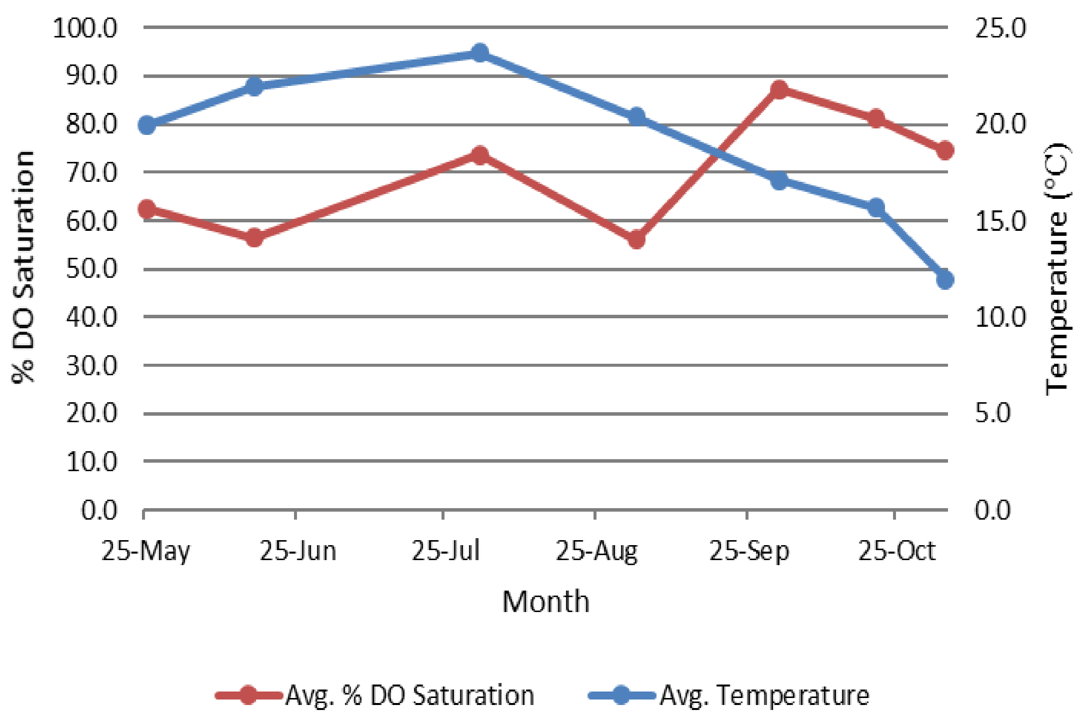

Figure 13 Percent dissolved oxygen saturation vs temperature, 2016. The blue line indicates baseline values and the red line indicates rain events.

Nutrients

No trends were observed for ammonia with respect to location within the watershed (Figure 14). Ammonia was repeatedly higher during the warmer months where farming and fertilizer use would be more frequent. As Li et al. (2014) found, livestock production is a dominant factor for total nitrogen and ammonium loadings. Agricultural areas produce greater ammonia loadings during the spring when cattle-rearing season begins, and early summer when farm land is actively plowed and seeds are planted. Ammonia did not seem to be highly impacted by rain events. This could be due to dispersion and dilution of ammonia in the stormwater runoff and as it travels downstream. According to the Spearman correlation, TSS, TS, TDS, TFS, total coliforms, and fecal coliform values were all statistically significant with ammonia. Ammonia negatively correlated with TSS, total coliforms, and fecal coliforms. In addition, there was a moderately strong positive correlation with TS, TDS, and TFS. ANOVA results showed statistical significance between ammonia and TDS. This is a result of nutrients, especially phosphorus, having the ability to attach to and persist in the sediment.

Soluble Reactive Phosphate (SRP) was generally higher at sites upstream than sites downstream (Figure 15). In congruence to results found by Matysik et al. (2014), who reported that higher concentrations of nutrients are found in areas where agricultural and urbanized land use predominate, sites in Columbiana County where agricultural land use was abundant had higher levels of phosphate than other sites. Upstream sites appeared to have increased SRP levels during months where events were sampled as opposed to months where baselines were taken. Because phosphorus is predominately found in agricultural fertilizers and manure, it can be concluded that agricultural upstream sites were more heavily affected by phosphorus in runoff than downstream sites. Spearman showed that TS, TDS, and TFS were statistically significant and shared a moderately strong positive correlation with SRP (Table 14). Leone et al. (2008) reported that phosphorus can be bound to sediments within water bodies which would support the correlation between SRP and solids. ANOVA results showed no statistical significance with any other variables (Appendix). In summary, nutrients were typically higher at upstream sites, where agricultural land use was dominant, than downstream sites.

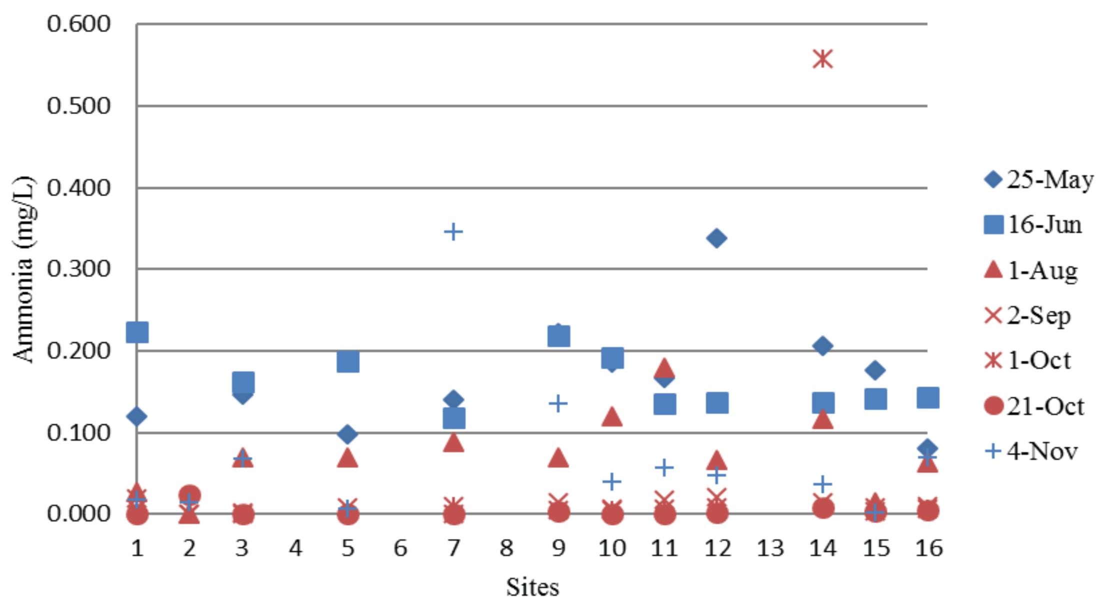

Figure 14 Average ammonia from sampling sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events

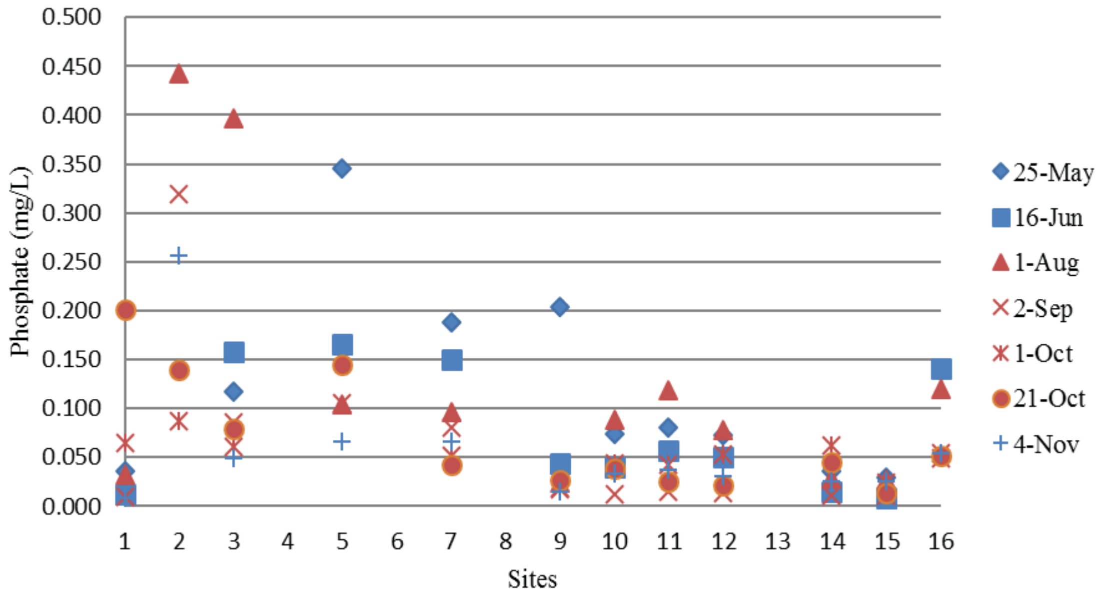

Figure 15 Average soluble reactive phosphate from sampling sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

Table 14: SPSS Spearman Output for ammonia and soluble reactive phosphorus (SRP) and

		Ammonia	SRP	TSS	TS	TDS	TVS	TFS	Total Coliforms	Fecal Coliforms	BOD
Ammonia	Correlation Coefficient	1.000	0.114	**-0.282	**0.377	**0.428	0.117	**0.282	**-0.372	**-0.373	-0.148
	Sig. (2-tailed)	.	0.148	0.000	0.000	0.000	0.140	0.000	0.000	0.000	0.060
	N	162	162	162	162	162	162	162	162	162	162
SRP	Correlation Coefficient	0.114	1.000	0.005	**0.249	**0.213	0.076	**0.408	-0.132	-0.137	-0.118
	Sig. (2-tailed)	0.148	.	0.950	0.001	0.006	0.338	0	0.094	0.082	0.135
	N	162	162	162	162	162	162	162	162	162	162

various water quality parameters, 2016.

**Correlation is significant at the p=0.01 level (2-tailed)

*Correlation is significant at the p=0.05 level (2-tailed)

Solids and Organic Matter

Upstream sites had total suspended solid (TSS) values generally higher than downstream after rain events (Figure 16). Solids can be affected by construction activities, which release large volumes of sediment into surface waters. In seasonally variable locations like Ohio, construction activities normally predominate in the summer and fall, which could possibly explain an increase in solids during warmer months. However, construction activities were not closely monitored throughout the project and cannot be heavily relied upon for interpreting the results. Total dissolved solids (TDS) and fecal coliforms were statistically significant with TSS with a moderate positive correlation (Table 15). Chudoba et al. (2013) found that additions of TSS can often result in an increase of bacteria in the water since many contaminants can attach to and persist in the sediment. ANOVA results showed no statistical significance with any other variable (Appendix).

Total solids (TS) were highest during baseline sampling in May and June (Figure 17). Trends were usually higher during baseline samples, which concludes that rain events did not have a pronounced effect on the number of total solids discharged into the river. While Line (2013) found that TSS did not correlate with the percentage of impervious surface, it is presumable that TS also does not correlate with the amount of impervious surface. Total solids enompass both TDS and TSS, which includes total fixed solids (TFS) and total volatile solids (TVS), giving rise to the strong correlation results. Spearman's corrlation shows that total solids strongly positively correlated with total dissolved solids at 0.948 and total fixed solids at 0.620 (Table 15). ANOVA showed statistical significance with TDS, TFS, and ammonia (Appendix). TS also moderately positively correlated with TVS and moderately negatively correlated with both total and fecal coliforms. TS may be negatively correlated with total and fecal coliforms due to its negative correlation with rain events, however, this is only speculation and requires further investigation.

Total dissolved solids (TDS) were highest during May and November and did not follow any specified upstream/downstream trend (Figure 18). TDS did not seem to be impacted by rain events due to higher numbers during baselines as opposed to rain events. Spearman correlation showed that TDS had a strong positive correlation with TFS and a significant moderate positive correlation with TVS. This is expected since these are all forms of solids. TDS had a moderate negative correlation with both total and fecal coliforms. TDS could have a negative correlation with total and fecal coliforms for the same reason that TS has a negative correlation with them: solids have a negative correlation with rain events where as coliforms do not. ANOVA showed statistical significance with TVS, TFS, and TS (Appendix).

Total volatile solids (TVS) values were highest in June and followed no general pattern (Figure 19). TVS is the volatile portion of TSS. During the Spearman correlation, TVS had a moderate negative correlation with TFS, total coliforms, and fecal coliforms. TVS had a negative correlation with TFS because these two solids added together equal TSS. If TVS increases, TFS decreases and vice versa. ANOVA results showed statistical significance with TDS and TFS (Appendix). TVS was not influenced by rain events. Total Fixed Solids (TFS) was greatest during May and, much like total volatile solids, followed no general pattern (Figure 20). TFS is the fixed portion of TSS. Baseline samples in May and June yielded greater values than the event samples, indicating that TFS was not affected by rain events. TFS had no statistically significant correlations with any parameters not previously mentioned in the results section, according to the Spearman correlation. ANOVA results showed statistical significance with TDS, SRP, and TS. TSS were the only solids that increased during months with significant rain events. All other solids were not affected by rain events and experienced higher values during baseline sampling. In summary, solids were predominately higher in the upstream sites where agricultural land use was dominant, than downstream sites.

Table 15: SPSS Spearman Output for solids and biochemical oxygen demand (BOD) and various water quality parameters, (TSS= total suspended solids, TS=total solids, TDS=total dissolved solids, TVS total volatile solids, TFS=total fixed solids)

		Ammonia	SRP	TSS	TS	TDS	TVS	TFS	Total Coliforms	Fecal Coliforms	BOD
TSS	Correlation Coefficient	**-0.282	0.005	1.000	-0.093	**-0.310	-0.010	-0.012	0.112	*0.170	0.061
	Sig. (2-tailed)	0.000	0.950	.	0.239	0.000	0.903	0.881	0.158	0.031	0.440
	N	162	162	162	162	162	162	162	162	162	162
TS	Correlation Coefficient	**0.377	**0.249	-0.093	1.000	**0.948	**0.362	**0.645	**-0.244	**-0.218	-0.063
	Sig. (2-tailed)	0.000	0.001	0.239	.	0.000	0.000	0.000	0.002	0.005	0.427
	N	162	162	162	162	162	162	162	162	162	162
TDS	Correlation Coefficient	**0.428	**0.213	**-0.310	**0.948	1.000	**0.312	**0.620	**-0.254	**-0.223	-0.065
	Sig. (2-tailed)	0.000	0.006	0.000	0.000	.	0.000	0.000	0.001	0.004	0.409
	N	162	162	162	162	162	162	162	162	162	162
TVS	Correlation Coefficient	0.117	0.076	-0.010	**0.362	**0.312	1.000	-0.035	*-0.201	**-0.247	-0.030
	Sig. (2-tailed)	0.140	0.338	0.903	0.000	0.000	.	0.662	0.010	0.002	0.702
	N	162	162	162	162	162	162	162	162	162	162
TFS	Correlation Coefficient	**0.282	**0.408	-0.012	**0.645	**0.620	-0.035	1.000	-0.127	-0.144	-0.070
	Sig. (2-tailed)	0.000	0.000	0.881	0.000	0.000	0.662	.	0.107	0.068	0.378
	N	162	162	162	162	162	162	162	162	162	162
BOD	Correlation Coefficient	-0.148	-0.118	0.061	-0.063	-0.065	-0.030	-0.070	0.023	*0.163	1.000
	Sig. (2-tailed)	0.060	0.135	0.440	0.427	0.409	0.702	0.378	0.724	0.011	.
	N	162	162	162	162	162	162	162	243	243	243

**Correlation is significant at the p=0.01 level (2-tailed)
*Correlation is significant at the p=0.05 level (2-tailed)

Biochemical oxygen demand (BOD) exhibited no observable trend in the data (Figure 21). The October 21 event sampling yielded the most consistently high values due to the high rainfall intensity. Arienzo et al. (2000) noted that runoff from urban settings can carry pet wastes and other organic material from impervious surfaces and fertilizers from residential lawns, which can increase the BOD five to ten times in nearby areas. During the October 21 event, BOD values were higher downstream where land use is mostly urban and residential. Equipment and holding time errors during early months of research could be responsible for sporadic data in May and June. The Spearman correlation showed no statistically significant correlation between BOD and any other variable measured, which suggests that BOD is not dependent on any other varible measured. No ANOVA was performed due to BOD having no statistical significance with any other variable.

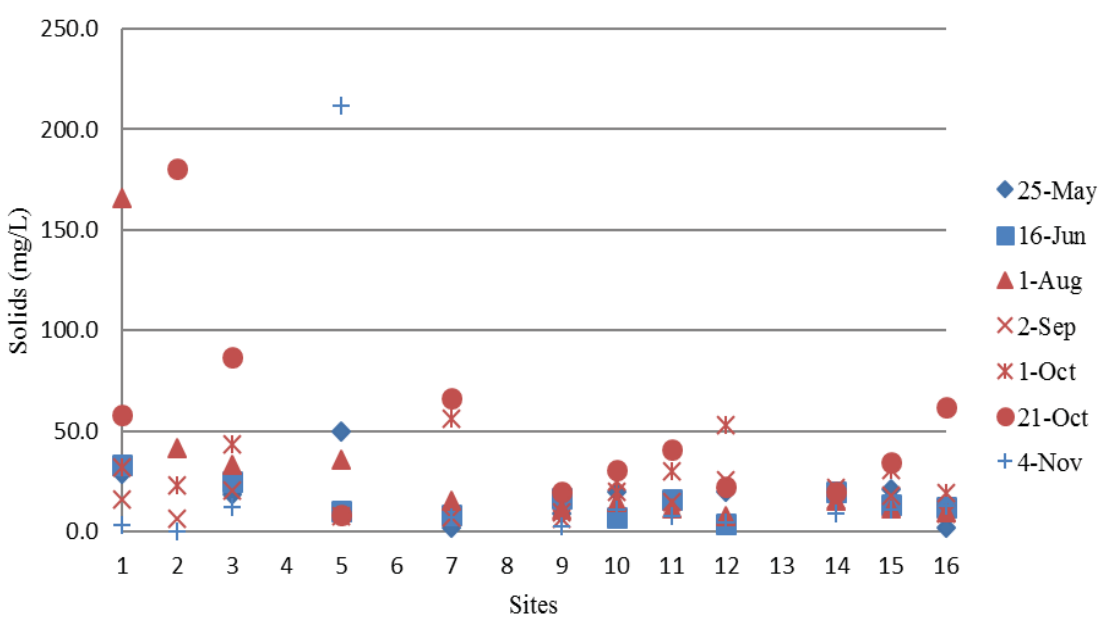

Figure 16 Average total suspended solids from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

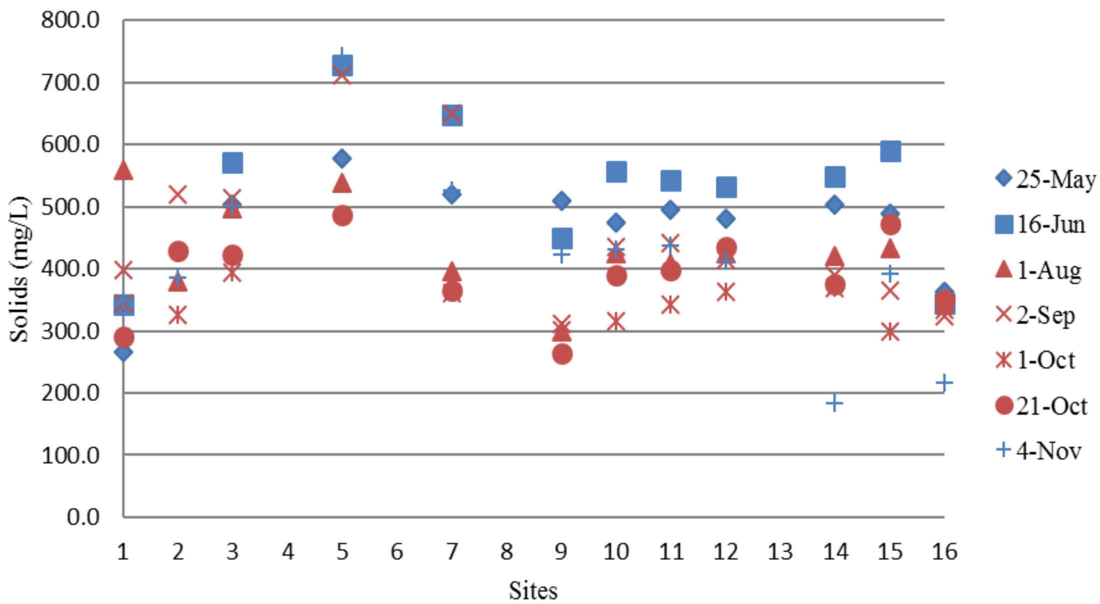

Figure 17 Average site total solids from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

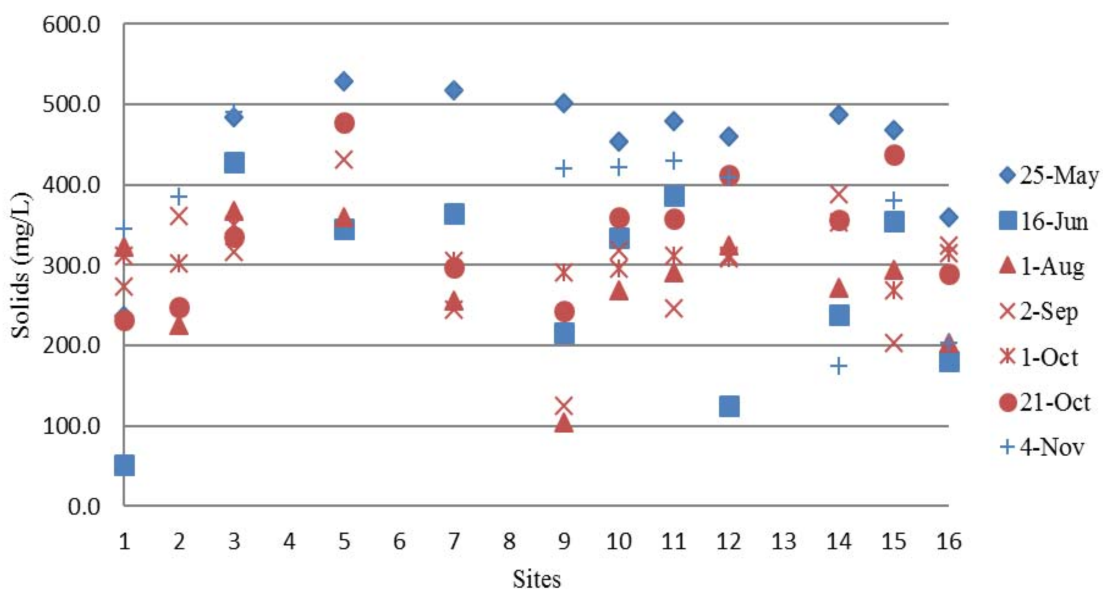

Figure 18 Average site total dissolved solids from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

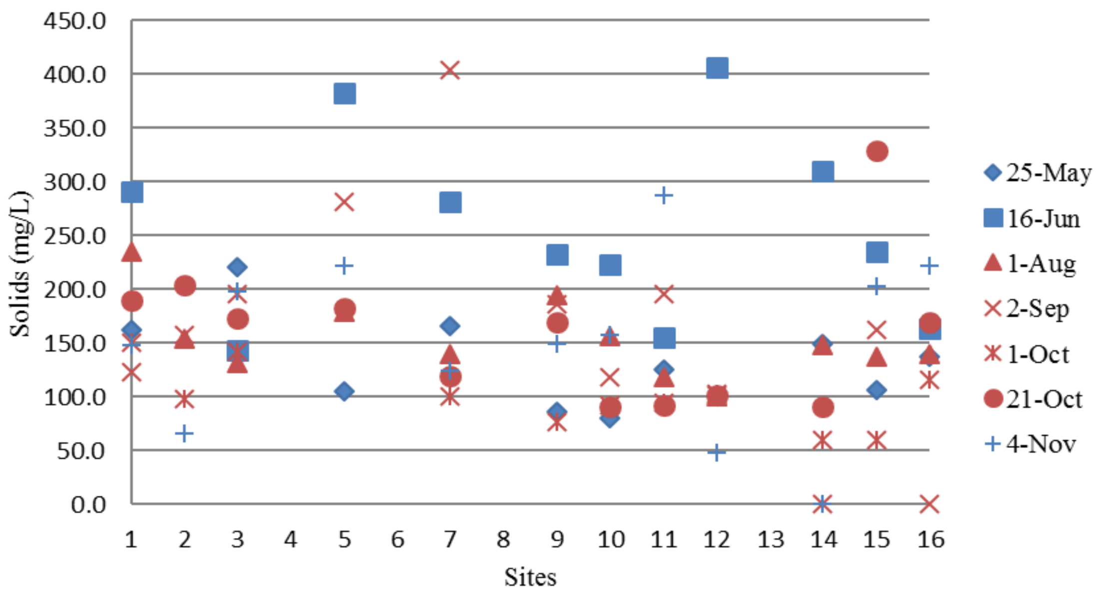

Figure 19 Average total volatile solids from sites in Mill Creek, 2016. Blue markers indicate basline values and red markers indicate rain events.

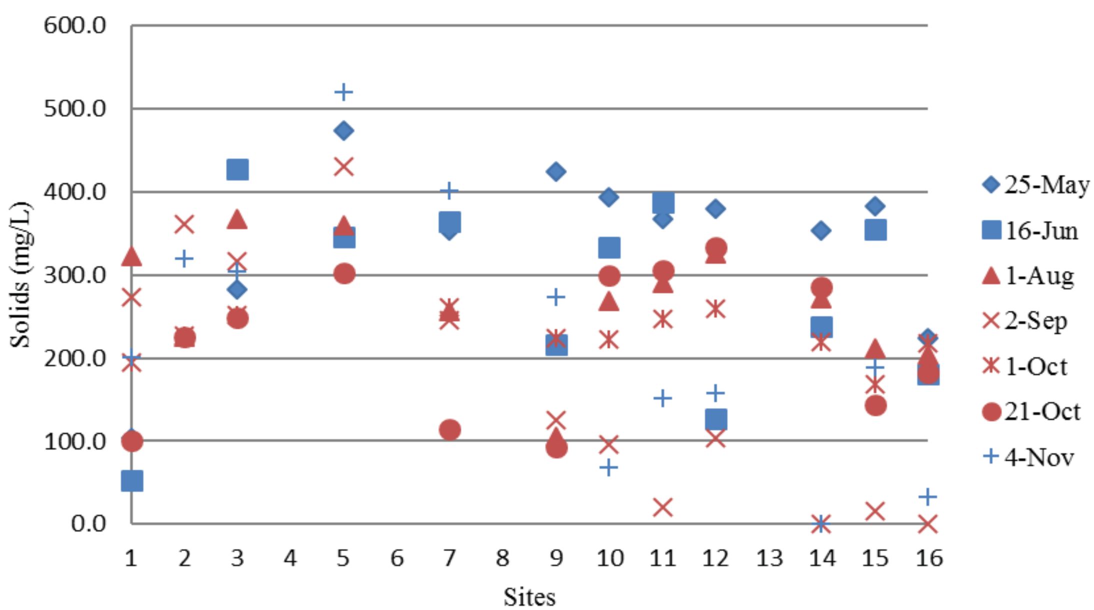

Figure 20 Average total fixed solids from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

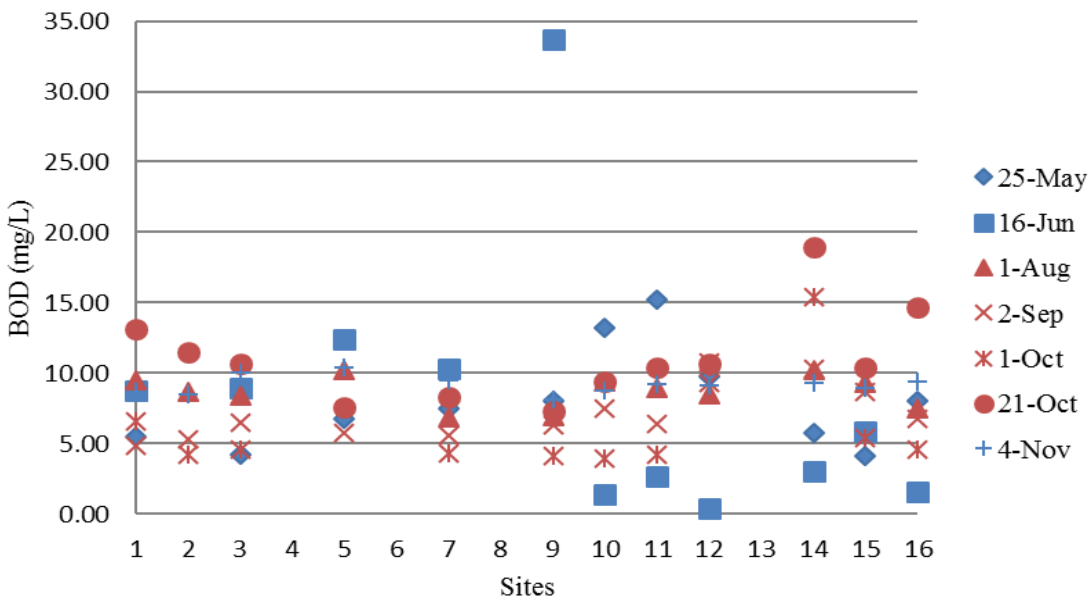

Figure 21 Average BOD from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

Coliforms

Total coliforms were somewhat impacted by rain events (Figure 22). The greater the amount of precipitation, the greater the observed number of total coliforms. Total coliforms experienced the greatest values during the October 21 sampling event where cumulative rainfall was 10.13cm. They are specifically highest at the first three sites, which are predominately agricultural land use, site 9, which is more residential, and site 16, which is largely industrial and residential land use. Total coliform bacteria include bacteria that is found in soil, surface waters, and fecal material. During a heavy rainfall, bacteria from the soil and fecal material resting near a river/stream's riparian zone is washed into surface waters by storm runoff drastically increasing coliform counts. Total coliforms were strongly positively correlated with the fecal coliforms group during the Spearman correlation suggesting that as total coliform numbers increase/decrease, fecal coliform numbers will follow the same trend (Table 16). ANOVA showed statistical significance with fecal coliforms and ammonia (Appendix). Total coliforms could have statistical significance with ammonia due to both nutrients and coliforms having the ability to persist in water body sediment as recognized by Chudoba et al. (2013). Similar to total coliforms, fecal coliform counts were higher during rain events and highest during the October 21 sampling event (Figure 23). These results mirrored those of Gannon and Busse (1989) who found that fecal bacteria concentrations were significantly higher in wet weather than dry weather. Also like total coliforms, fecal coliform counts during that event were highest at the first three sites as well as sites 9 and 16. Fecal coliform numbers are also influenced by the amount of precipitation an area receives. As observed by Sanders et al. (2013), periods of increased streamflow from rainfall are positively correlated with fecal bacteria concentrations. Because fecal coliforms are a sub-group of total coliforms, they will uaually mirror the increases/decreases that total coliforms exhibit. Due to the subgroup factor, fecal coliforms exhibited the greatest positive correlation with total coliforms in regards to the Spearman correlation. ANOVA results showed statistical significance with total coliforms for the same reason (Appendix).

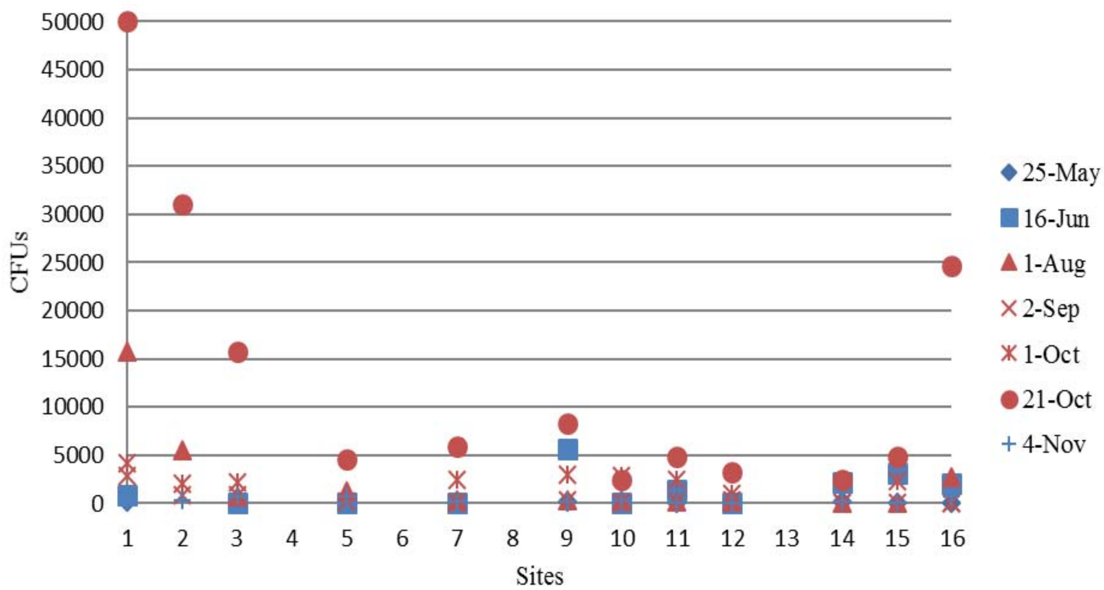

Figure 22 Average total coliforms from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

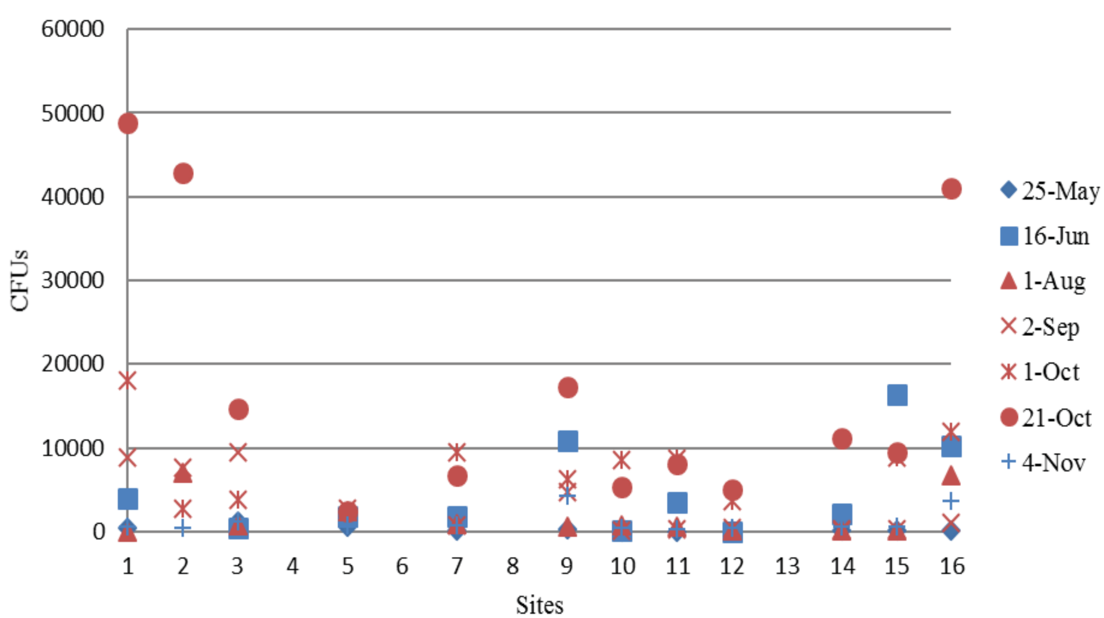

Figure 23 Average fecal coliforms from sites in Mill Creek, 2016. Blue markers indicate baseline values and red markers indicate rain events.

Metals were tested from October 1 to November 4. Many elements were in such minute quantities that they were removed from the final table due to irrelevance. Elements that were found in larger quantities included calcium, potassium, magnesium, sodium, phosphorus, and sulfur. Tchounwou et al. (2014) found that heavy metal pollution results predominately from point sources such as mining, foundries and smelters, and other industrial processes. This lead to the expectation that metal levels would be higher downstream due to the increasing percentage of industrial and urban land use. However, results showed these downstream metal values were not notably higher than upstream levels (Appendix).

Table 16 SPSS Spearman Output for total and fecal coliforms and various water quality parameters.

		Ammonia	SRP	TSS	TS	TDS	TVS	TFS	Total Coliforms	Fecal Coliforms	BOD
Total Coliforms	Correlation Coefficient	**-0.372	-0.132	0.112	**-0.244	**-0.254	*-0.201	-0.127	1.000	**0.482	0.023
	Sig. (2-tailed)	0.000	0.094	0.158	0.002	0.001	0.010	0.107	.	0.000	0.724
	N	162	162	162	162	162	162	162	324	324	243
Fecal Coliforms	Correlation Coefficient	**-0.373	-0.137	*0.170	**-0.218	**-0.223	**-0.247	-0.144	**0.482	1.000	0.163*
	Sig. (2-tailed)	0.000	0.082	0.031	0.005	0.004	0.002	0.068	0.000	.	0.011
	N	162	162	162	162	162	162	162	324	324	243

**Correlation is significant at the p=0.01 level (2-tailed)
*Correlation is significant at the p=0.05 level (2-tailed)

Overall Analysis

Areas of agricultural land use did result in higher concentrations of nutrients, fecal coliforms, and solids as was hypothesized. Areas of urban and industrial land use did have increased quantities of total and fecal coliforms, but areas of agricultural land use had greater quantities of coliforms. Predominant metals found within the watershed included calcium, potassium, magnesium, sodium, phosphorus, and sulfur, however, these values are most likely due to the geology of the area, which is high in limestone.

Chapter 5 Conclusion

This research suggests that many contaminants are deposited into the Mill Creek watershed via many different land uses surrounding the watershed area. Sampling was conducted from May 2016 to November 2016. Both field and laboratory parameters were measured at baseline and following precipitation events. Soluble reactive phosphorus was most prevalent upstream (Columbiana County) where land use is predominately agricultural. Total and fecal coliforms counts were greatest during precipitation events. Following precipitation events, coliform counts were highest, specifically upstream where agricultural land use dominated and in the Mahoning River (site 16). Precipitation events did not appear to influence any parameters other than total and fecal coliforms. Greater efforts are recommended to protect watershed quality starting with a more intensive monitoring of farms and other agricultural lands in Columbiana County. Steep sloped areas, CSOs, and areas with direct connections to livestock waste must be more closely monitored during rainfall events to prevent the introduction of contaminants to surface waters. In addition, construction stormwater management would reduce the amount of sediment released into surface waters from construction activities. Results of this project will aid Mill Creek MetroParks and the Mahoning County District Board of Health and help to improve management of waters coming into and leaving the park. Furthermore, sampling protocol has been established and monorting in the Mill Creek watershed will continue for several more years. It is suggested that sampling be expanded into some of the tributaries to further identify land use influences.

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Appendix

ICP Results

Table 17 ICP Results in ppm

Site #	Date	Rep	Aluminum	Barium	Calcium	Iron	Potassium	Magnesium	Manganese	Sodium	Nickel	Phosphorus	Sulfur	Vanadium	Tungsten
1	1-Oct	1	0	.0437	52.70	0	9.828	12.76	0	19.53	0	.1846	11.88	.0029	.1004
1	1-Oct	2	0.0439	.0416	51.74	0	9.640	12.51	0	19.20	0	.1846	11.69	.0088	.1575
1	21-Oct	1	0.0726	0	27.84	0	12.79	7.411	.0019	7.030	.0767	.5109	5.260	0	.0007
1	21-Oct	2	0.1015	0	27.49	0	12.78	7.364	.0010	6.992	.0764	.4982	5.257	0	.0005
1	4-Nov	1	0	0.0545	68.16	.0732	5.311	16.24	0	22.93	0	.0208	14.32	.0080	.0664
1	4-Nov	2	0	.0533	66.83	0	5.250	15.95	0	22.43	0	.0163	14.21	.0050	.0926
2	1-Oct	1	0.0356	.0372	49.74	0	5.705	10.85	.0004	33.25	0	.2291	13.63	.0117	.1794
2	1-Oct	2	0	.0375	50.54	0	5.801	10.99	0	33.81	0	.2287	13.77	.0102	.2407
2	21-Oct	1	0.0128	0	29.08	0	8.479	6.244	.0018	14.90	.0764	.3062	6.866	.0008	0
2	21-Oct	2	0.0233	0	29.04	0	8.279	6.240	.0011	14.88	.0762	.3104	6.888	0	.0011
2	4-Nov	1	0	.0499	78.59	.0004	5.937	17.49	0	57.87	0	.6297	21.76	.0177	.1440
2	4-Nov	2	0	.0501	78.49	0	5.882	17.28	0	57.81	0	.6198	21.71	.0048	.0771
3	1-Oct	1	0	0	49.00	0	6.134	13.15	0	29.84	.0787	.1454	27.40	0	0
3	1-Oct	2	0	0	48.36	0	5.944	12.81	0	29.40	.0792	.1492	26.19	.0032	.0002
3	21-Oct	1	0	0	42.89	0	6.871	11.81	.0033	26.51	.0791	.1843	23.35	0	0
3	21-Oct	2	0	0	42.68	0	6.789	11.73	0	26.33	.0791	.1808	23.26	0.0029	0
3	4-Nov	1	0.072	.0367	86.67	0	5.045	23.05	.0011	44.83	0	.1158	45.26	.0047	.1035
3	4-Nov	2	0.0907	.0375	88.75	.0678	5.062	23.14	.0049	44.98	0	.1259	45.10	.0073	.1212
5	21-Oct	1	0	0	42.85	0	9.506	8.476	0	73.19	.0768	.3418	25.32	.0018	0
5	21-Oct	2	0	0	42.96	0	9.429	8.522	0	73.82	.0769	.3385	25.07	.0016	.0006
5	4-Nov	1	0.0491	.0247	80.30	0	6.537	20.34	.0030	67.32	0	.1637	42.24	.0117	.0293
5	4-Nov	2	0.0676	.0246	81.00	0	6.599	20.53	.0038	67.88	0	.1636	42.60	.0031	0
7	1-Oct	1	0	0	39.12	0	5.260	9.213	0	36.81	.0772	.1270	18.22	0	.0026
7	1-Oct	2	0	0	38.71	0	5.503	9.091	0	36.39	.0769	.1183	17.72	0	.0002
7	21-Oct	1	0	0	30.76	0	4.664	6.360	0	35.82	.0766	.0880	11.52	.0012	0
7	21-Oct	2	0	0	30.54	0	4.694	6.310	0	35.59	.0767	.0865	11.59	0	0
7	4-Nov	1	0.0146	.0273	77.88	0	7.373	19.13	0	78.80	0	.1703	37.89	.0082	.0675
7	4-Nov	2	0.0254	.0263	78.11	0	7.389	19.07	0	79.16	0	.1695	37.54	.0102	.2401
9	1-Oct	1	0.0268	.0106	36.49	0	4.275	6.933	0	54.20	0	.0413	13.03	.0083	.1125
9	1-Oct	2	0.0365	.0107	36.62	0	4.353	6.954	0	54.31	0	.0463	13.20	.0078	.1298
9	21-Oct	1	0	0	27.24	0	3.809	5.384	0	38.57	.0759	.0554	9.217	0	0
9	21-Oct	2	0	0	27.13	0	3.676	5.373	0	38.40	.0758	.0526	9.164	0	0
9	4-Nov	1	0.007	.0303	66.51	0	4.825	13.65	0	80.53	0	.0279	17.59	.0120	.0709
9	4-Nov	2	0	.0312	67.16	0	4.913	13.80	0	81.23	0	.0287	17.67	.0105	.1000
10	1-Oct	1	0.0392	.0147	39.33	.1054	5.973	8.741	.0004	40.40	0	.1328	16.83	.0107	.2083
10	1-Oct	2	0.0392	.0144	39.48	.0126	6.029	8.765	.0017	40.61	0	.1228	16.92	.0073	.0926
10	21-Oct	1	0	0	40.40	0	5.143	9.332	.0042	50.15	.0770	.0808	19.43	0	0
10	21-Oct	2	0	0	40.10	0	5.098	9.244	0	49.53	.0762	.0771	18.56	0	0
10	4-Nov	1	0.0057	.0221	67.69	0	5.988	16.37	.0066	66.30	0	.0869	31.15	.0070	.1196
10	4-Nov	2	0.012	.0220	67.11	0	6.053	16.31	.0084	65.72	0	.0879	31.29	.0042	.1389
11	1-Oct	1	0.0232	.0133	39.01	0	5.608	8.663	0	41.29	0	.1209	16.38	.0140	.1921
11	1-Oct	2	0.0139	.0132	38.91	0	5.548	8.644	0	41.27	0	.1220	16.37	.0033	.0859
11	21-Oct	1	0	0	43.18	0	5.446	10.45	0	56.45	.0765	.0451	21.76	0	0
11	21-Oct	2	0	0	43.37	0	5.723	10.53	0	56.82	.0763	.0443	22.08	0	0
11	4-Nov	1	0.0136	.0216	64.68	0	5.723	15.67	0	64.09	0	.0880	29.59	.0091	.2136
11	4-Nov	2	0.0083	.0223	65.04	0	5.858	15.77	.0011	64.42	0	.0894	29.87	.0090	.0987
12	1-Oct	1	0.0657	.0122	36.79	.0277	5.121	7.872	0	40.43	0	.1483	15.01	.0097	.1839
12	1-Oct	2	0.0785	.0121	37.12	.0240	5.029	7.921	.0005	40.84	0	.1526	15.17	.0134	.1282
12	21-Oct	1	0	0	46.48	0	5.927	11.53	.0032	61.44	.0790	.0353	24.82	0	0
12	21-Oct	2	0	0	46.72	0	5.718	11.59	0	61.55	.0769	.0402	24.92	0	0
12	4-Nov	1	0	.0222	62.73	0	5.691	15.03	.0019	61.60	0	.0828	27.90	.0023	.0575
12	4-Nov	2	0.0138	.0225	62.47	0	5.662	14.96	.0028	61.36	0	.0810	27.82	.0193	.1380
14	1-Oct	1	0.0392	.0183	45.27	0	5.076	10.17	.0175	50.93	0	.2201	20.92	.0090	.1584
14	1-Oct	2	0.0453	.0174	45.17	0	5.038	10.13	.0240	50.90	0	.2169	20.65	.0045	.1334
14	21-Oct	1	0	0	43.15	0	4.795	11.14	.0173	42.62	.0769	.1034	20.37	.0016	0
14	21-Oct	2	0	0	43.14	0	4.718	11.12	.0039	42.59	.0764	.1002	20.18	0	0
14	4-Nov	1	0.0052	.0217	61.01	0	5.662	14.74	0	58.20	0	.0636	25.74	.0076	.1334
14	4-Nov	2	0.0198	.0218	61.18	0	5.669	14.73	0	58.35	0	.0635	25.72	.0081	.0332
15	1-Oct	1	0.0665	.0106	34.67	0	4.261	7.182	.0008	41.22	0	.0763	14.14	.0063	.1245
15	1-Oct	2	0.048	.0113	35.06	0	4.430	7.278	.0004	41.75	0	.0776	14.37	.0104	.1817
15	21-Oct	1	0	0	47.53	0	5.672	11.97	0	60.35	.0768	.0203	26.22	.0025	0
15	21-Oct	2	0	0	47.14	0	5.624	11.89	0	59.93	.0767	.0210	26.01	0	0
15	4-Nov	1	0.086	.0228	59.81	0	5.269	14.01	.0058	58.39	0	.0609	25.57	.0183	.1193
15	4-Nov	2	0.0559	.0210	59.46	0	5.435	14.03	0	58.87	0	.0649	25.55	.0105	.1286
16	1-Oct	1	0.0506	.0146	37.72	0	4.842	9.661	.0006	43.91	0	.1837	16.13	.0092	.1566
16	1-Oct	2	0.0254	.0123	37.60	0	4.798	9.637	.0006	43.87	0	.1752	16.12	.0196	.0070
16	21-Oct	1	0	0	33.83	0	5.122	8.734	.0034	36.89	.0770	.1107	16.96	.0016	0
16	21-Oct	2	0	0	33.80	0	5.163	8.697	.0143	36.88	.0769	.1202	16.87	.0041	0
16	4-Nov	1	0.048	.0178	47.81	0	6.248	14.13	.0049	40.22	0	.1528	22.63	.0113	.1193
16	4-Nov	2	0	.0162	47.46	0	6.065	14.03	.0036	39.86	0	.1501	22.59	.0131	.1762

SPSS Data and Results

Table 18 Ammonia SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TS	Between Groups	1269799.232	87	14595.393	1.325	0.107
	Within Groups	814836.545	74	11011.305		
	Total	2084635.778	161			
TDS	Between Groups	1335860.591	87	15354.719	1.531	0.03
	Within Groups	742244.477	74	10030.331		
	Total	2078105.068	161			
Total Coliforms	Between Groups	570283.780	87	6554.986	0.944	0.604
	Within Groups	513974.720	74	6945.604		
	Total	1084258.500	161			
Fecal Coliforms	Between Groups	397878.635	87	4573.318	0.919	0.65
	Within Groups	368352.803	74	4977.741		
	Total	766231.438	161			

Table 19 SRP SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TFS	Between Groups	1715812.294	91	18855.08	1.218	0.195
	Within Groups	1083411.533	70	15477.308		
	Total	2799223.827	161			

Table 20 TSS SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TDS	Between Groups	684212.762	56	12218.085	0.92	0.629
	Within Groups	1393892.306	105	13275.165		
	Total	2078105.068	161			

Table 21 TS SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TDS	Between Groups	2006100	102	19668	16.115	0
	Within Groups	72005.5	59	1220.4		
	Total	2078105	161			
TVS	Between Groups	1087053	102	10657	1.146	0.287
	Within Groups	548879.5	59	9303		
	Total	1635933	161			
TFS	Between Groups	2090121	102	20491	1.705	0.013
	Within Groups	709102.5	59	12019		
	Total	2799224	161			
Ammonia	Between Groups	1.169	102	0.011	1.668	0.017
	Within Groups	0.405	59	0.007		
	Total	1.575	161			

Table 22 TDS SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TVS	Between Groups	1412534.605	124	11391.408	1.887	0.014
	Within Groups	223398.333	37	6037.793		
	Total	1635932.938	161			
TFS	Between Groups	2435852.16	124	19643.969	2	0.008
	Within Groups	363371.667	37	9820.856		
	Total	2799223.827	161			
TS	Between Groups	2045832.778	124	16498.651	15.732	0
	Within Groups	38803	37	1048.73		
	Total	2084635.778	161			
TSS	Between Groups	170223.105	124	1372.767	1.309	0.174
	Within Groups	38803	37	1048.73		
	Total	209026.105	161			
Ammonia	Between Groups	1.173	124	0.009	0.87	0.718
	Within Groups	0.402	37	0.011		
	Total	1.575	161			

Table 23 TVS SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TDS	Between Groups	1448449.41	88	16459.652	1.908	0.002
	Within Groups	629655.658	73	8625.42		
	Total	2078105.068	161			
TS	Between Groups	1397834.011	88	15884.477	1.688	0.011
	Within Groups	686801.767	73	9408.243		
	Total	2084635.778	161			

Table 24 TFS SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
TDS	Between Groups	1448449.41	88	16459.652	1.908	0.002
	Within Groups	629655.658	73	8625.42		
	Total	2078105.068	161			
TS	Between Groups	1397834.011	88	15884.477	1.688	0.011
	Within Groups	686801.767	73	9408.243		
	Total	2084635.778	161			

Table 25 Total Coliforms SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
Fecal Coliforms	Between Groups	1164984.08	103	11310.525	2.535	0
	Within Groups	981572.177	220	4461.692		
	Total	2146556.256	323			
Ammonia	Between Groups	0.735	60	0.012	1.475	0.043
	Within Groups	0.839	101	0.008		
	Total	1.575	161			

Table 26 Fecal Coliforms SPSS ANOVA Output

		Sum of Squares	df	Mean Square	F	Sig.
Total Coliforms	Between Groups	1725315	102	16915	4.471	0
	Within Groups	836145.4	221	3783.5		
	Total	2561460	323			
Ammonia	Between Groups	0.704	66	0.011	1.163	0.248
	Within Groups	0.871	95	0.009		
	Total	1.575	161			

Coliforms and Precipitation with sampling date

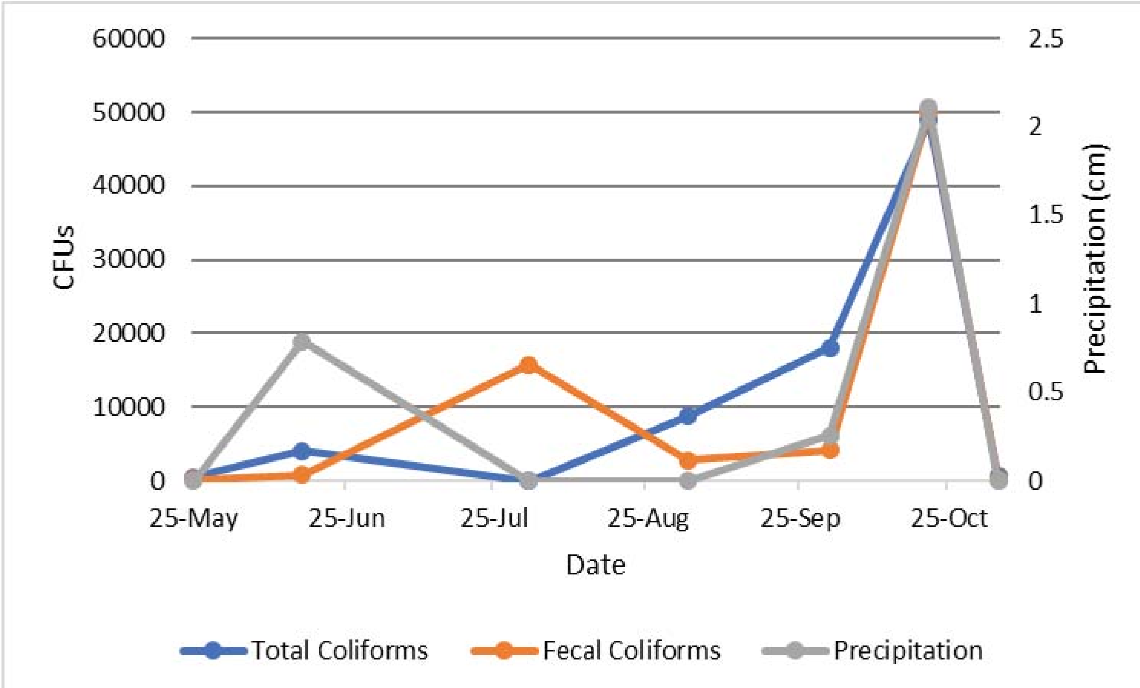

Figure 24 Site 1 Coliforms and Precipitation with sampling date

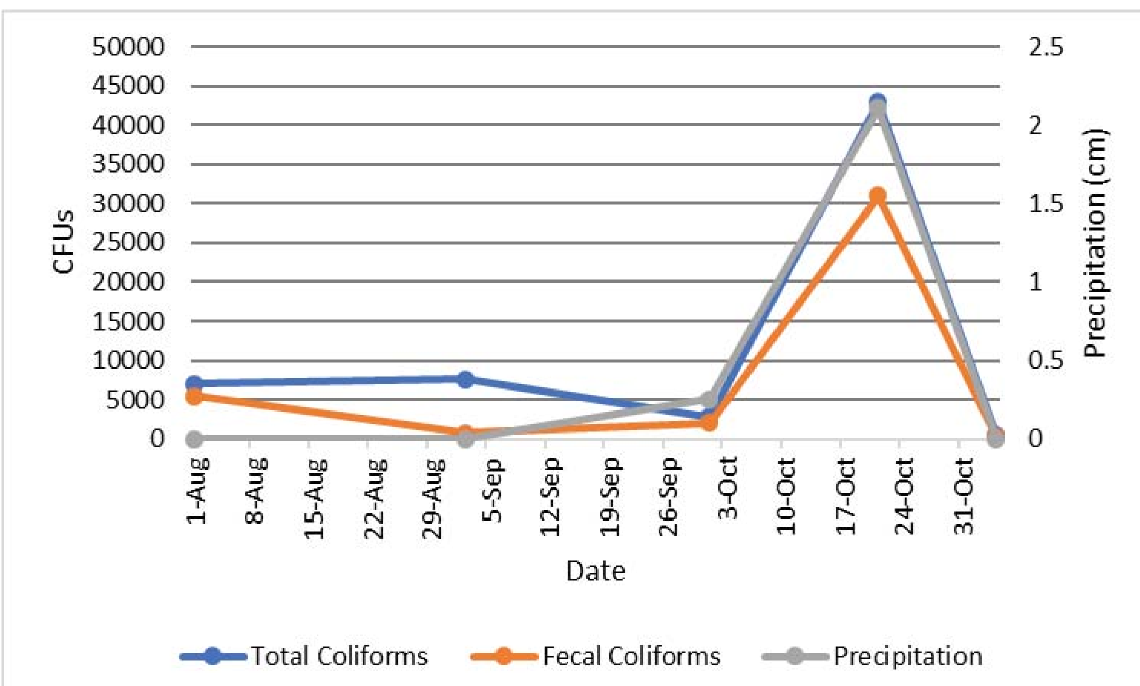

Figure 25 Site 2 Coliforms and Precipitation with sampling date

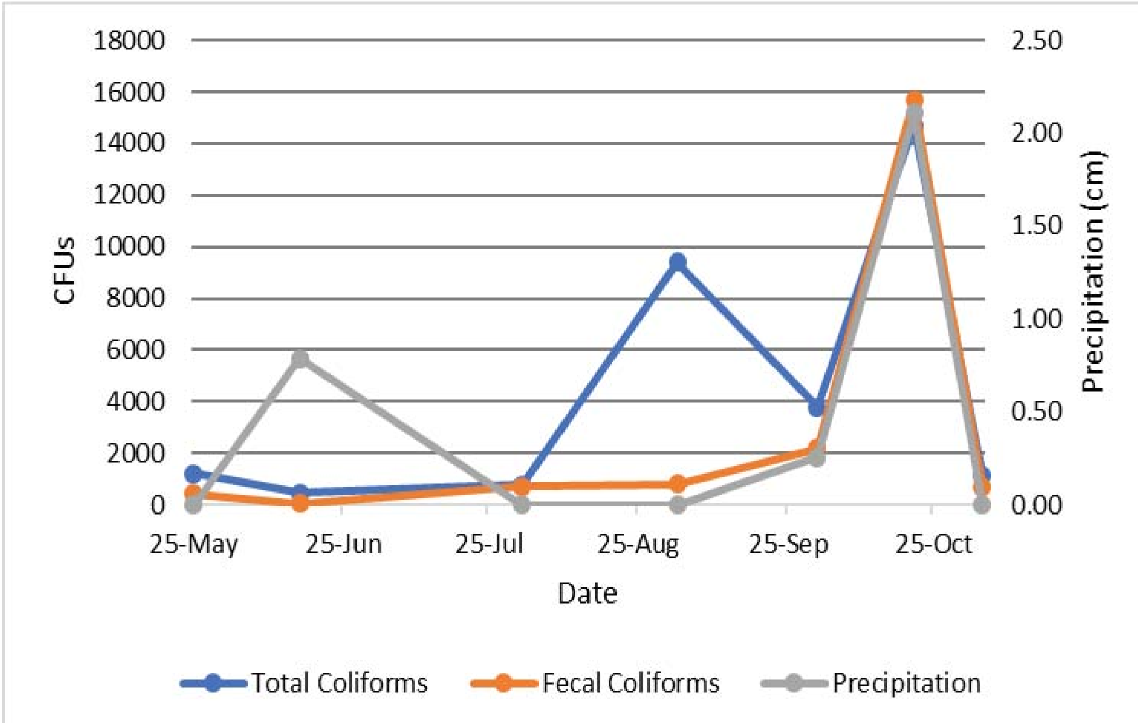

Figure 26 Site 3 Coliforms and Precipitation with sampling date

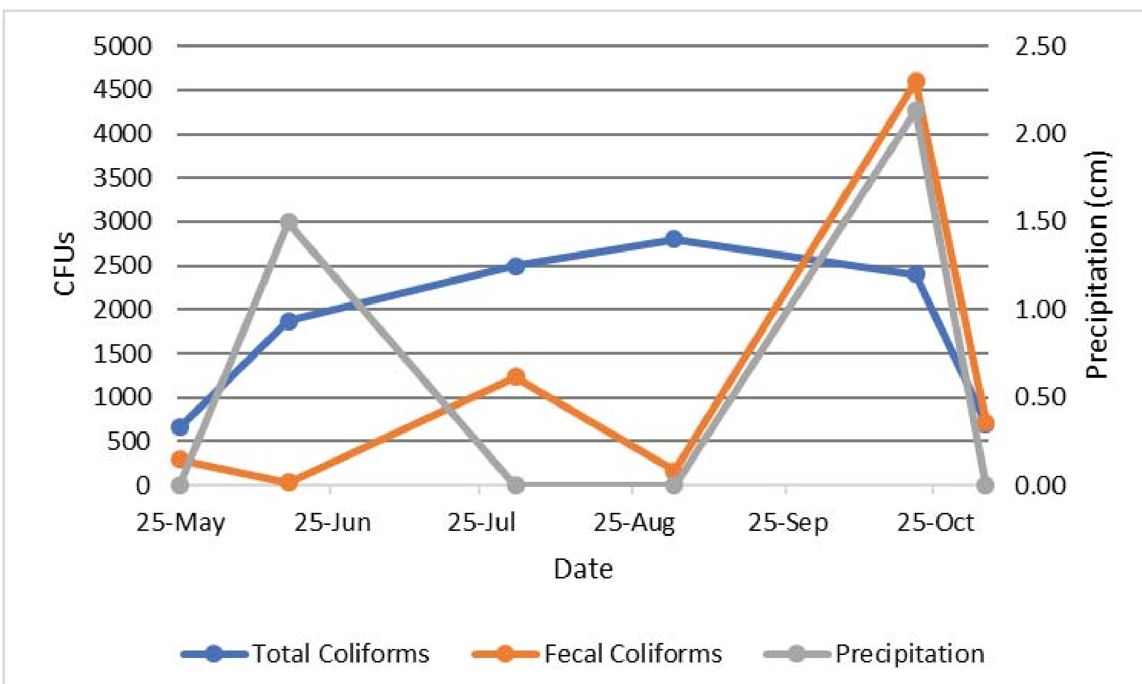

Figure 27 Site 5 Coliforms and Precipitation with sampling date

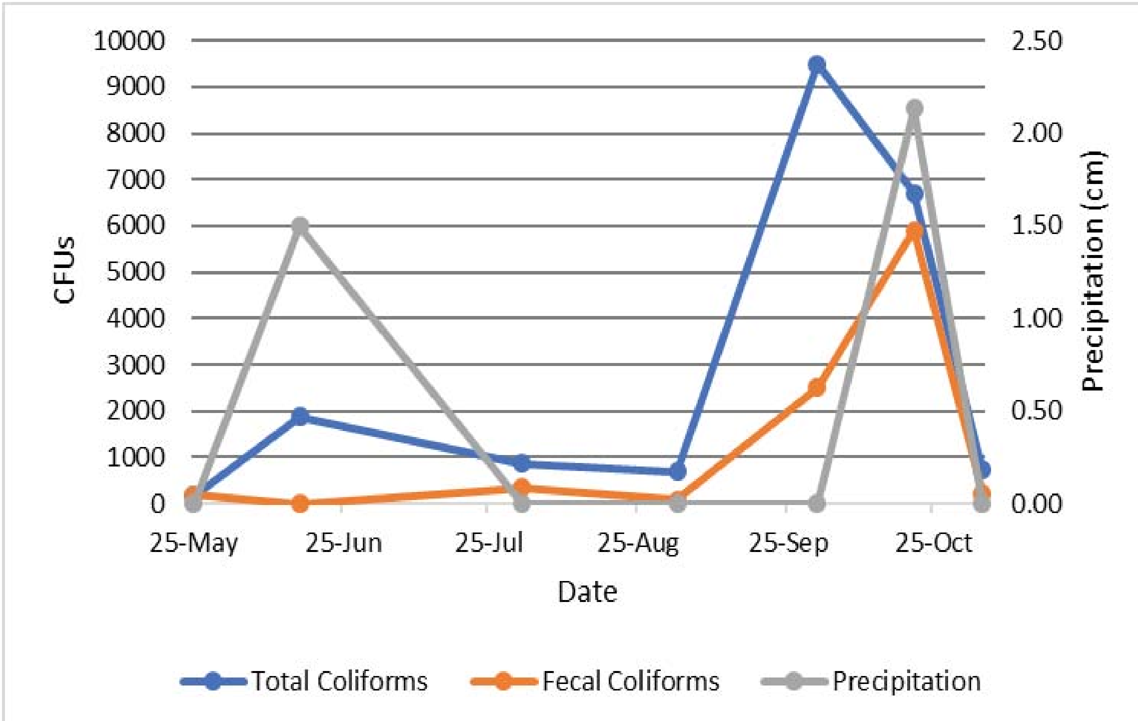

Figure 28 Site 7 Coliforms and Precipitation with sampling date

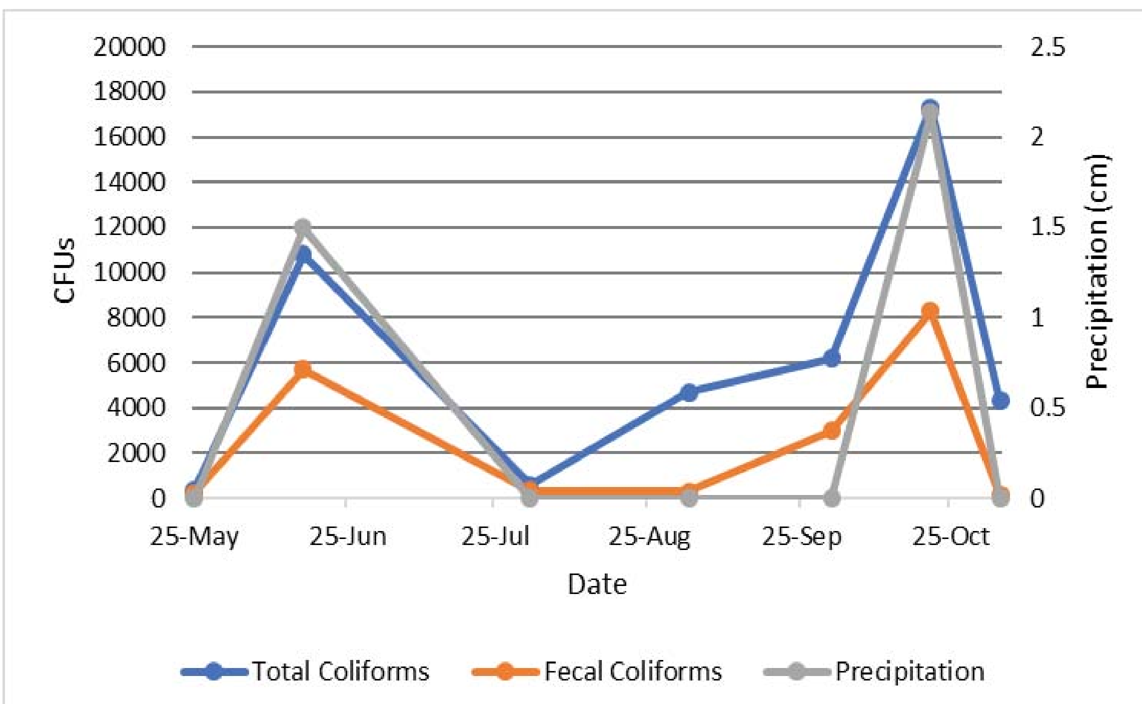

Figure 29 Site 9 Coliforms and Precipitation with sampling date

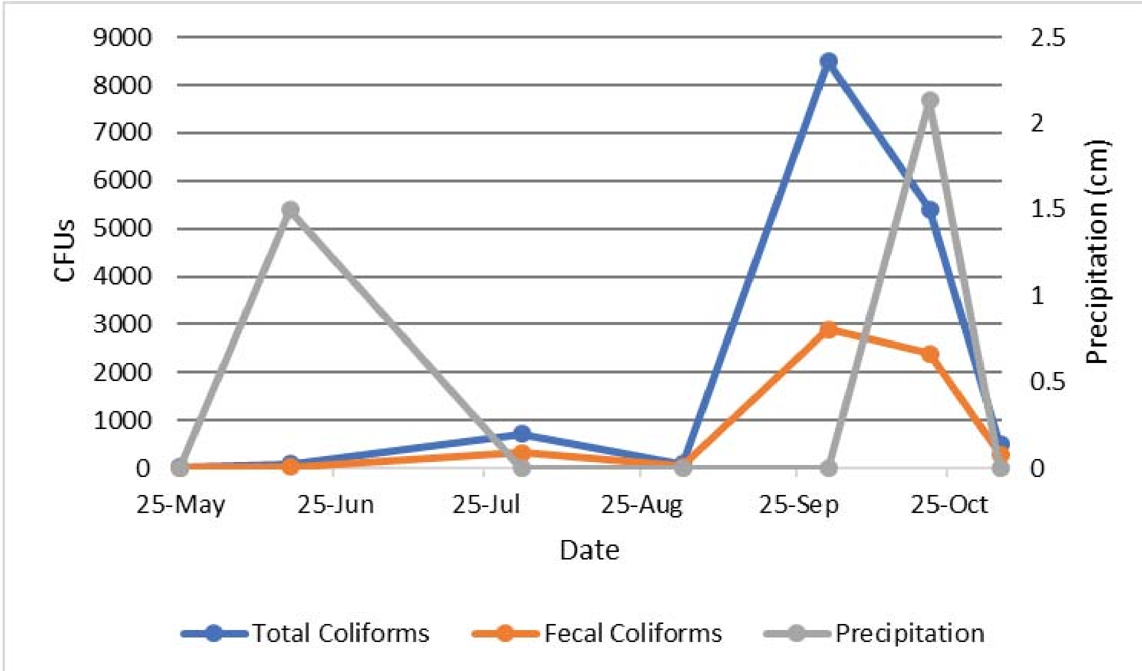

Figure 30 Site 10 Coliforms and Precipitation with sampling date

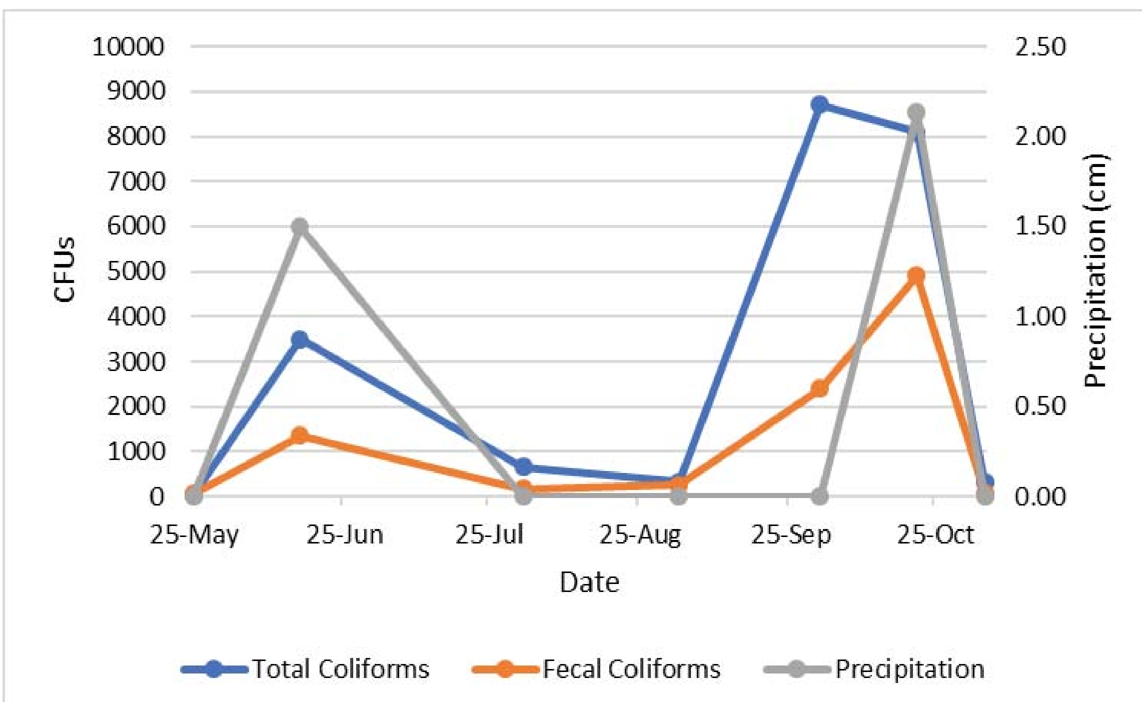

Figure 31 Site 11 Coliforms and Precipitation with sampling date

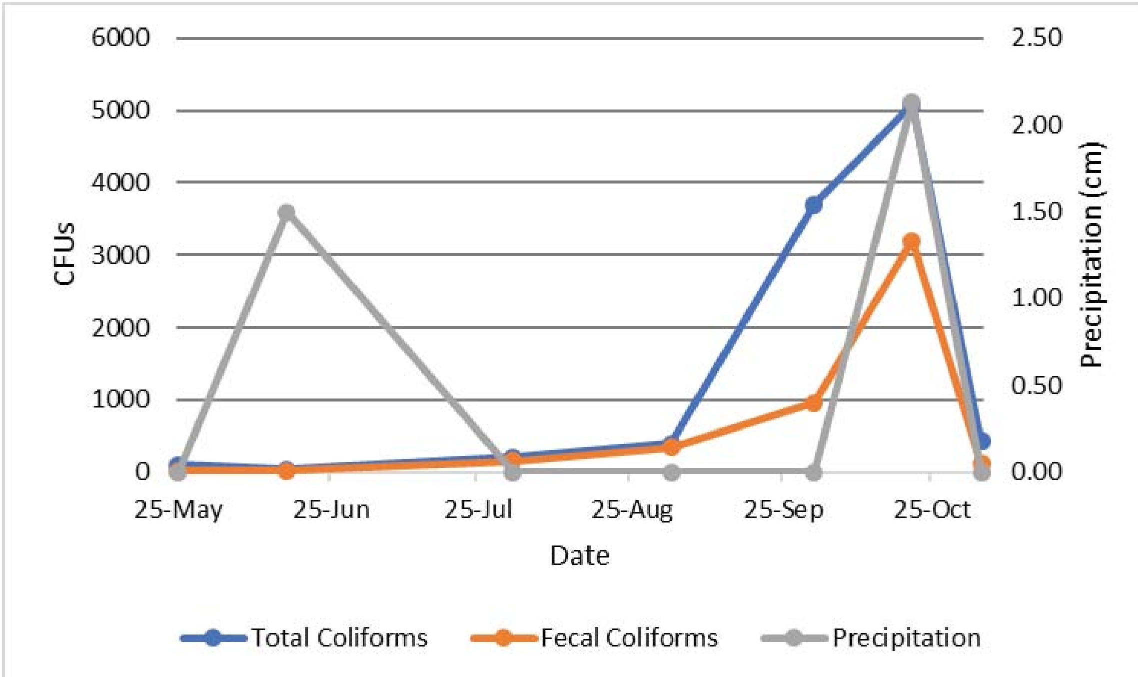

Figure 32 Site 12 Coliforms and Precipitation with sampling date

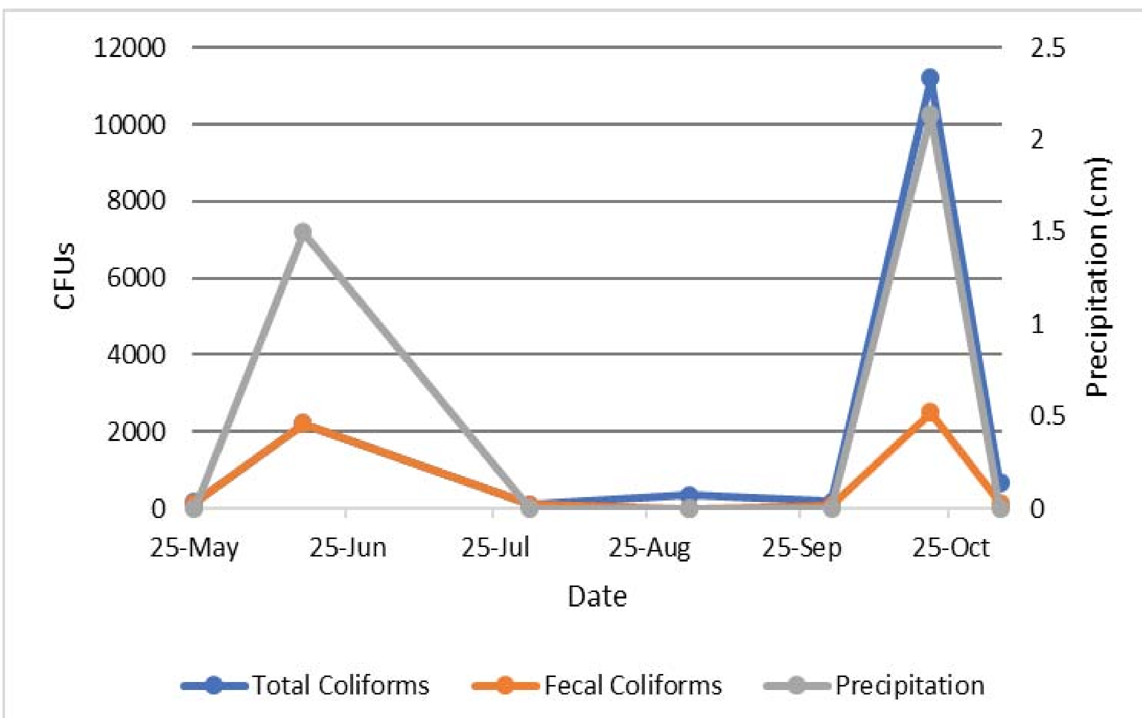

Figure 33 Site 14 Coliforms and Precipitation with sampling date

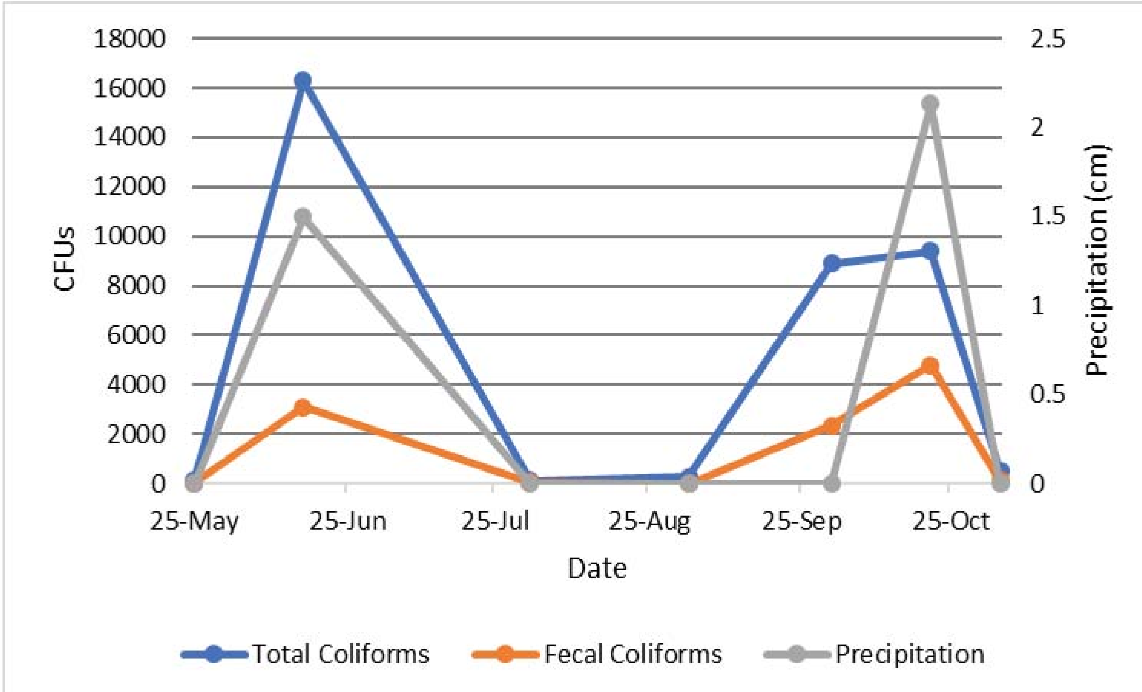

Figure 34 Site 15 Coliforms and Precipitation with sampling date

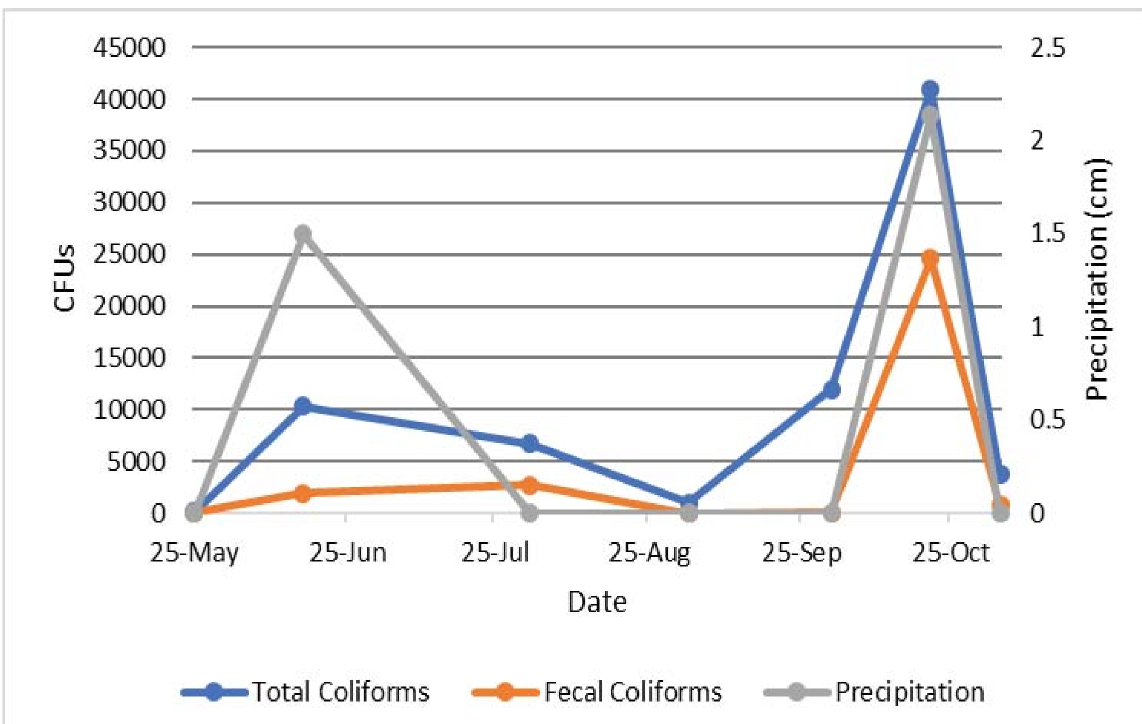

Figure 35 Site 16 Coliforms and Precipitation with sampling date