

AN EVALUATION OF ENVIRONMENTAL HEALTH THREATS ASSOCIATED WITH STREAM DISCHARGE FROM TOWN CREEK IN GREENVILLE, NORTH CAROLINA

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Town Commons is a major recreational area within the city of Greenville that is frequented by many students and residents who utilize the water resources of the Tar River for kayaking, fishing and other activities. Complaints of gasoline odors and oily substances in Town Creek, near Town Commons have been documented since the 1980's and these complaints persist today. Also, storm water runoff has been identified as major non-point source of pollution due to the high percentage of impervious surface (~50%) in the Town Creek Watershed. The North Carolina Department of Environmental and Natural Resources indicated that groundwater contaminated by leaking underground storage tanks (LUST) was likely discharging into Town Creek and causing the odor and aesthetic issues. Excess bacteria concentrations in the recreational waters, especially after rain events, may be a public and environmental health threat. The goal of this study was to determine if the discharge from Town Creek poses a threat to the environment and public health. The specific objectives included: 1) to determine if the benzene concentration in groundwater and surface water exceeded the national standards (51 µg/L); 2) to

determine if the air quality standard for benzene was exceeded near Town Creek (5 ppm for 15 or more minutes); and 3) to determine if the concentrations of *E. coli* and enterococcus exceeded the recreational water quality standards (single sample threshold, 235 cfu/100 mL for *E. coli* and 61 cfu/100 mL for enterococcus). Results showed that benzene concentrations in water were higher than standards for 40% of the sampling events, benzene concentrations in the air were higher than standards 75% of the sampling events and *E. coli* concentration in the stream were higher than standards 40% of the time during base flow and 75% during storm flow.

Implementation of storm water control measures, remediation of groundwater contaminated with benzene, and continued monitoring is suggested to improve the quality of water in Town Creek.

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STREAM DISCHARGE FROM TOWN CREEK IN GREENVILLE, NORTH CAROLINA

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I. Introduction & Background

Reports dating back to the 1980's from the NC Department of Environment and Natural Resources (currently known as DEQ) indicated that groundwater and soil were contaminated with benzene from leaking underground storage tanks (LUSTs) in the Town Creek watershed, (Figure 1). In May 1992, the North Carolina Department of Environmental and Natural Resources notified Greenville Utilities Commission that no responsible parties were identified as the source of benzene contamination, but landowners where the contamination exists may be liable; ECU and the City of Greenville were on the list of property owners. Town Creek was later listed as a Low Priority Site and since 1996 there have been no remediation efforts, just some infrequent monitoring. However, recent monitoring data collected on June 10, 2015 showed that along portions of the western banks of Town Creek where groundwater upwells (seeps), the concentration of benzene in air was between 0.1 and 1.0 ppm (1000 ppb). The benzene-contaminated water from seeps along the stream bank was flowing into Town Creek and then into the Tar River near Town Commons where people launch canoes and participate in other water-based recreational activities.

In addition to leaking underground storage tanks, urban runoff from streets has collectively impaired the water quality in Town Creek. (S&ME, 2011). The Town Creek watershed has a high percentage of impervious areas (~ 50%), which consists of buildings, parking lots and roads, which can increase the amount of runoff. Urban runoff can transport pathogenic bacteria from fecal matter from animals and humans to surface waters. Humans can be exposed to pathogens through ingestion or skin contact while swimming, which may result in skin infections, gastroenteritis or other ailments (Perdek, et. al., 2003). Studies have shown that gastrointestinal disorders can also result from the ingestion of raw shellfish growing in

contaminated waters (Perdek, et. al., 2003). Therefore excess bacteria concentrations in surface waters are public and environmental health threats.

1.1 Benzene and Groundwater Contamination

Driving is a daily routine for many people. As urbanization increases, there is a corresponding increase in the number of vehicles on the road. Following World War II, there was a surge in the number of automobiles, which resulted in the construction of many gas stations (Meegoda & Hu, 2011). Gas station owners installed large capacity underground storage tanks made of steel, to store the fuel. These tanks were connected to fuel pumps. Storage tanks were buried underground to reduce fire hazards and to save space (Hayward, 1994). However, the tanks do not last forever, and when the tanks start to corrode, fuel can leak into the ground and may contaminate soil and groundwater. Since the tanks are buried, leakage may occur unnoticed for years. On average, the life expectancy of steel tanks, depending on the corrosion, is about thirty to fifty years (Meegoda & Hu, 2011). Tanks that are improperly installed and operated may leak even if they are relatively new. When the leaks are discovered, then it is the responsibility of the station owner to remediate the problem, but in some instances stores close down, leaving behind the leaking tanks and contamination. This can pose significant threats to environment and public health. For example, fuel spills can disrupt ecosystems and have detrimental effects on plants and animals (Meegoda & Hu, 2011). Also the leaking tanks increase the risk of fire and explosion if vapors from the leak travel through sewer lines and then into buildings (Meegoda & Hu, 2011). One major concern with storage tanks leaking is groundwater contamination. Many people obtain their drinking water from groundwater wells and if groundwater becomes contaminated with fuel, public health is at risk. Whenever there is a possible storage tank leak, it is important that this be rectified in a timely manner because many

people could be exposed to the fuel putting their health in danger. Many leaks are not discovered until a large volume of fuel has contaminated groundwater. Finding the origin of the contamination in urban areas with many potential sources is expensive and may take several years.

1.2 Constituents of Gasoline

Underground storage tanks (USTs) contain petroleum, which is a mixture of hydrocarbon constituents that includes benzene, toluene, ethyl benzene and xylenes (Johnson et. al., 2003). This complex mixture can also be referred to as BTEX compounds. The compounds are significant when it comes to pollution because each can have harmful effects on the environment and the public if exposure occurs. BTEX compounds are the most soluble and most significant in terms of pollution potential (Johnson et. al., 2003). Once a leak occurs there is a good chance that all the compounds will be released into the ground and possibly make their way to ground water. The most soluble of all the hydrocarbons is benzene, which is a well-known genotoxic carcinogen. It is a simple organic compound, which occurs naturally in the environment but in low concentrations (Duarte-Davidson et. al., 2001). Toluene and ethyl benzene are not considered to be causes of cancer and even though xylenes can have detrimental effects on the kidneys, liver and nervous system, it is not as hazardous as the other compounds (Meegoda & Hu, 2011). Due to its toxicity, benzene is somewhat more important than the other compounds in regards to contamination of groundwater. Less than 2% of petroleum is made up of benzene but it is the most persistent of all the petroleum components (Johnson et. al., 2003). Benzene occurs naturally also in crude oil and is a constituent of petrol (Duarte-Davidson, et. al., 2001).

The molecular structure of benzene makes it relatively resistant to degradation and oxidation, allowing it to persist in the environment (Johnson et. al., 2003). Toluene, ethyl

benzene and xylene all have different characteristics that allow them to degrade quicker than benzene, and thus they do not persist in the environment as long. The degradation process of these compounds can be inhibited by various environmental factors. For example, it appears that BTEX compounds break down more rapidly in aerobic conditions (Johnson et. al., 2003). The degradation process of BTEX slows or in some instances can actually come to a halt in low redox potential aquifers. The addition of oxygen to contaminated aquifers can be a costly and difficult operation. The only way to effectively oxygenate groundwater is through continuous sparging which requires installation of expensive remediation and monitoring equipment on wells to ensure sufficient oxygen is delivered to the area of contamination (Major, et. al., 1988).

Throughout the years, the EPA has made changes to laws and regulations to try and reduce exposure to benzene. In 2007, there was a regulation set forth that would reduce the amount of benzene in gasoline and set more restricted emission standards. It constituted 1% of gasoline in 2004 and the new regulation would reduce that level to on average 0.62%. Benzene poses the second-highest risk of developing cancer for Americans (Eilperin, 2007). Having the government actually stepping in and implementing tighter restrictions will assist in the process of decreasing exposure to benzene. This decrease in exposure will hopefully reduce the occurrence of people developing cancer from benzene.

1.3 Hazardous Waste Laws and Regulations

Once groundwater has been contaminated, the fuel storage tank owners may face enormous expenditures to clean up the site, as well as compensating injured parties. In 1980, Congress passed the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), sometimes referred to as Superfund Act, to address abandoned waste sites. This allowed the Environmental Protection Agency (EPA), to take action against owners of sites that

pose substantial endangerment to public health (Jenkins et. al., 2006). The CERCLA assigns financial responsibility to responsible parties. In 1984, when Congress added Subtitle I to the Solid Waste Disposal Act, it authorized the UST program, thereby enforcing the Environmental Protection Agency to develop regulatory programs for USTs storing hazardous substances (Rubrecht, 2012). This amendment would assist in ensuring that the environment would be protected by law in case of accidental leakage. The EPA promulgated regulations for new USTs in 1988. Under the regulations, it required that new storage tanks be designed and installed to prevent leaks and also required existing tanks to be upgraded. Owners and operators were also required to demonstrate financial responsibility, monitor and report any releases and clean up any releases. At a Senate hearing in late 1988, the assistant EPA administrator of Water, Jack E. Raven, estimated that there were 75,000 to 100,000 tanks leaking more than 41.5 million Liters of gas annually (Hayward, 1994). This had the potential to become a major problem. All tanks that were installed after December 22, 1988 had to meet at least one of the following performance standards to prevent corrosion: tanks and piping had to be made of non-corrodible material, those made of steel had to have corrosion-resistant coating and those installed without corrosion protection had to have an expert determine that the environment was not corrosive (EPA, 2015). The federal government was determined to ensure the safety of the public. Congress passed the Energy Policy Act of 2005 and also amended Subtitle I of the Solid Waste Disposal Act (Rubrecht, 2012). The amendments required operators to complete special trainings related to fuel spills and regulations. To ensure that the appropriate party would be held responsible in case of a leak, an ownership change notification had to be completed within thirty days of the change. Most polluting activities were now regulated by detail federal statutes, with the enactment of the Clean Water Act, the Resource Conservation and Recovery Act and the

Clean Air Act. To assist storage tank owners, the EPA distributes a chemical advisory on how to detect, avoid and repair a leak (Hayward, 1994). Storage tank owners have been provided with ample tools to assist in the prevention of storage tanks leaking. Like most laws, UST regulations are enforced by both federal and state agencies through penalties and administrative orders. An owner may be confronted with enforcement action, which requires them to comply with remediation procedures and also pay government penalties.

When UST owners do not comply with regulations there can be harsh punishments. For example, in 1992 Coastline Purchasing Corp. were fined for \$141,722 by the EPA for various violations. They were fined because their five USTs were not emptied and inspected and they did not have leak-detection devices on their tanks (Hayward, 1994). There has been federal programs set up to assist with clean up. These come in handy when UST owners abandon contaminated sites. The Leaking Underground Storage Tank Trust Fund, which is administered by the UST program, pays for cleanups in these cases. It has been reported that as of 2005, of the 450,000 confirmed leaks from tanks, 350,000 has been successfully cleaned up (Jenkins, et. al., 2006).

Most actions against tank owners arise under state administrative law since it was designed for states to implement. For the most part, states have incorporated the federal government's minimum standards rather than establishing stricter standards. During the late 1990s, states were encouraged to implement a risk-based approach to corrective programs. By adopting this approach it would improve consistency throughout the states in cleanup prioritization (Jenkins, 2006). Each state has their own way of dealing with inspections and enforcements. For example, South Carolina implemented its own enforcement staff. This differs from the approach Pennsylvania and Wisconsin takes because they both use third-party inspectors that verifies if storage tanks are in compliance. Ohio uses a method of placing decals

on storage tanks and those that lack said decal are not able to be filled. Here in North Carolina, we use a similar approach (Geyer, 1998).

1.4 Health Hazards Associated with Benzene Exposure

Benzene is recognized as a known carcinogen and recent concern has focused on continuous exposure of benzene at low environmental concentrations. A major health risk that has been linked with exposure to benzene in low concentrations is non-lymphocytic leukemia. The national contact standard for benzene concentrations in surface water is 51 µg/L (NC DENR, 2007) and the standard for drinking water is 5 µg/L (5 ppb) (FDA, 2015). Ingestion of benzene contaminated water is the most direct route of exposure and highly soluble products are readily absorbed through the gastrointestinal tract. Exposure may also occur via skin contact by swimming or wading in contaminated water. Studies have shown an increase likelihood of acute non-lymphocytic leukemia in people that were exposed via inhalation of benzene when concentrations in the air range are as low as 32-80 mg/m³ (32-80 µg/L) (Duarte-Davidson, et. al., 2001). Repeated exposure of more than 320 mg/m³ (320 µg/L) can result in aplastic anemia, pancytopenia, and is associated with a decrease in cells in bone marrow. Even at repeated exposures to concentrations less than 96 mg/m³ (96 µg/L) cytopenia can also develop (Duarte-Davidson, et. al. 2001). Those that are affected may be at risk of death due to a decrease in white blood cells. According to the Agency for Toxic Substances and Disease Registry, exposure to vapor or liquid can cause irritation to the eyes, skin and respiratory tract in humans (US CDC, 2014). Dermal exposure may result in redness or blistering of the skin. Studies on animals have shown immunologic, hematologic, and neurologic effects through oral exposure. Based on hematological effects on humans, the reference concentration is 0.03 mg/m³ (0.03 µg/L). This is

an estimate of inhalation exposure on a continuous basis that is more likely to be without appreciable risk of deleterious non-cancer effects (EPA, 2012). This reference concentration can be defined as an estimate of continuous inhalation exposure that is likely to be “without appreciable risk deleterious non-cancer effects over a lifetime” (EPA, 2012).

Increased exposure has been attributed to refueling at gas stations, as well as exposure in vehicles (Duarte-Davidson, et. al., 2001). Exposure rates vary depending on the benzene content of fuel, the time spent refueling and also if vapor control devices are in place (Duarte-Davidson, et. al., 2001). Inhalation of benzene can be problematic for those exposed to vapors. In a 1993 study conducted by MRC Institute for Environment and Health, University of Leicester, to evaluate exposure at filling stations, 72 service stations were monitored. The highest concentrations for those exposed were on average $482 \mu\text{g}/\text{m}^3$ ($0.482 \mu\text{g}/\text{L}$) with 52% being exposed on average to $320 \mu\text{g}/\text{m}^3$ ($0.320 \mu\text{g}/\text{L}$) (Duarte-Davidson, et. al., 2001). If the concentrations are high enough, there may be serious consequences. For example, inhaling benzene can have acute toxic effects on one’s nervous system and at concentrations between 800 and $1600 \text{ mg}/\text{m}^3$, headaches, vertigo, drowsiness and nausea have all been reported (Duarte-Davidson, et. al., 2001). There are two ways that exposure to a particular substance can be calculated. The first includes personal monitoring over a specific time period as one moves between microenvironments. The second is to measure typical concentrations in relevant microenvironments and relating that to the time and activity pattern of various populations in each microenvironment (Duarte-Davidson, et. al. 2001).

1.5 Groundwater Remediation

In the event of a leaking UST, gasoline may percolate through the soil to groundwater. When gasoline floats on the surface of groundwater, it is important that it is removed as soon as possible. The longer that it lingers, the better the chance that it migrates into drinking water wells. The petroleum floating on the groundwater surface is referred to as Light Non-Aqueous Phase Liquid and its thickness varies as the water table falls and rises (EPA, 2015). Gasoline can be removed from groundwater by active or passive collection equipment, chemically oxidized in situ or through excavation (EPA, 2015).

The ability to find potential groundwater contamination in a timely manner is key to reducing the chances of the placing the public's health at risk. Over the years the federal government has implemented various programs to assist with the cleanup of contaminated sites, as well as making sure those responsible were held liable. Through collaborative efforts with industry, territorial, state, and tribal partners, the EPA works to clean up releases from USTs. The EPA (2015) has estimated that there have been over 528,000 releases from USTs and about 72,000 sites that have yet to be cleaned. Contaminated sites can eventually make water unsafe to drink and can also be a fire hazard. There are techniques that can be used to help decrease the occurrences of leaks. One such technique is spill protection, which includes containment that goes around the fill pipe. Containment basins can catch small spills that may occur during the delivery of gasoline. A delivery hose can carry up to 52 liters of fuel, which can sometimes leak during this process. Some spill buckets may be equipped with pumps or drains to remove liquids caught during the filling process or unforeseen leaks (EPA, 2015). The fuel and sediments captured in the containment buckets must still be disposed of properly. A new requirement from the EPA in 2005 stated, "Not later than October 13, 2018, spill buckets must be either double walled (with periodic monitoring of the integrity of both walls of the spill bucket) or tested

periodically for proper operation according to the new spill prevention equipment testing requirements” (US EPA, 2015). By enacting regulations like this one, owners will have to make sure their tanks are in accordance with requirements, which will help prevent spills.

Corrosion is a major problem with some of the older storage tanks. Corrosion begins as pitting develops and creates holes in the metal. Over time, even a small hole in an UST can have a significant impact on the environment. The tank itself is not the only part at risk of corrosion, as other corrosion prone metal components includes swing joints, piping and flexible connectors (US EPA, 2015). Today the most common methods that are used to protect from corrosion are isolating metal components from the corrosive environment and cathodic protection (US EPA, 2015). Rules and regulations that have been implemented over the years have been designed to protect public health and the environment by ensuring that preventable measures are taken to place to reduce the occurrence of accidental leaks.

The Department of Environment and Natural Resources (DENR) (which is now known as The Department of Environmental Quality) has been making progress towards cleaning leaking underground storage tanks. As of March of 2009, DENR reported that 18,469 LUSTs sites have been cleaned; this represents 74 percent of the known releases in the state (Office of Underground Storage Tanks, 2011). However, at the time the data was collected, there were 6,343 releases still in the state’s backlog. Older releases make up the majority of the backlog. The EPA analyzed North Carolina’s LUSTs because it has one of the ten largest backlogs in the country (EPA, 2011). The state has so many sites in the backlog because many releases are complex and they take significant time and funding to clean. Due to limited resources, North Carolina has statutes that require DENR to address highest risk releases first and prohibits working on sites that are considered a lower risk until all high-risk releases have been addressed.

Groundwater contamination tends to be more dispersed than soil contamination, which helps support the idea that groundwater contamination takes longer to remediate than soil contamination. Backlogs within North Carolina have been divided up into 7 regions (Asheville, Winston-Salem, Mooresville, Fayetteville, Raleigh, Washington and Wilmington) with Greenville located in the Washington region (Figure 2, Table 1). Groundwater contamination comprises 95 percent of the releases in the Washington area in comparison to 62 percent in the Asheville area (Office of Underground Storage Tanks, 2011). The difference with these numbers may be due to hydrogeological variations between the two. The Washington region has coastal areas with shallow depths to groundwater and extensive aquifer systems, while the Asheville area is more mountainous with deeper water tables and a rock fracture systems for conveying groundwater. Asheville was determined to have depths to groundwater typically greater than 30-35 feet (Eimers et al., 2002), while the Washington area may have groundwater less than 5 feet deep. Areas that are more urbanized tend to have more automobiles, fueling stations and LUST releases than rural areas. For example, the Raleigh, Mooresville, and Winston-Salem regions have twice as many releases as each of the other regions (Table 1).

1.6 Town Creek and Benzene Contamination

On April 11, 1986, a resident of Greenville reported a persistent gasoline odor in the area around Town Creek. The Greenville Fire Department investigated the area and discovered a seep along the banks of town creek that appeared to be discharging gasoline products into the creek. The Greenville Fire Department notified the NC Department of Environmental and Natural Resources (NCDENR), who later conducted five phases of assessment activities (S&ME, 2011).

The North Carolina Department of Environment and Natural Resources conducted an onsite visit on April 29, 1986 to evaluate the complaints of contamination. During the site visit,

NCDENR discovered there were five potential sources of petroleum hydraulically up-gradient from the contaminated seep. These included Stop Shop, Fast Fare, University 66, Steve Horne Property and Pokegama. Over the next ten years there would be five assessment phases conducted by NCDENR to try and identify the source of the contamination. Phase I activities took place in May and June of 1986, during which NCDENR installed twelve monitoring wells (MW-1 through MW-12) for groundwater sampling and characterization. While the wells were being installed, it was reported that there was a gasoline odor in groundwater from many of the wells. By the conclusion of Phase I, data from the monitoring wells indicated that Fast Fare was a possible source (S&ME, 2011).

Phase II included the installation of 10 more monitoring wells in the watershed during the months of August and September. Out of all the twenty-two wells that were installed, all but three contained contaminant concentrations that were above regulatory standards. In the Phase II report NCDENR concluded, “It is with some degree of certainty that both the Stop Shop (during 1984-1985) and the University 66 (during 1977 or 1978) are known to have contributed to the gasoline seepage” (Receptor Survey and Soil and Groundwater Assessment Report, 2005). This conclusion was brought about after studies found contamination of monitoring wells in the area. In October of 1986, twenty-seven underground storage tanks were identified within 2,000 feet of the seep and ranged from 1060 to 37,854 liters (280 to 10,000 gallons) in size. Twenty of the twenty-seven USTs were no longer in use. University 66 had five USTs removed on November 5th and 6th due to the expansion of an office building. There was waste oil and heating oil USTs on site that had holes and line leakage but there was no evidence gasoline was released. Stop Shop, another possible source had its 18,900 liter UST removed in February of 1987 after

showing evidence of leakage and failure. Soil samples were taken and two fiberglass USTs were installed (S&ME, 2011).

The goal of Phase III was to identify and separate potential up-gradient sources of benzene. Three additional monitoring wells were installed (25 total in the watershed) around the Stop Shop and no contaminant compounds were shown in samples that were collected on November 30, 1987. These three additional wells were installed to the southwest, northwest and south of the Stop Shop (MW-23 through MW-25). All 25 temporary monitoring wells from the previous wells were reportedly abandoned between December 3rd and 9th of 1987 (S&ME, 2011).

Phase IV of assessment activities were completed to determine if USTs on the Steve Horne property could be contributing sources of contamination to Town Creek. Three monitoring wells were installed on Steve Horne property and soil samples were collected on October 12, 1988. No volatile organic compounds were detected in the soil or from the wells. This would suggest that the USTs on this property were not a source of the contamination. On April 15th of 1988, the Washington Regional Office issued a Notice of Noncompliance to the parent firm of Fast Fare, Crown Central Petroleum Corporation (Crown). Omni Environmental Services Inc. removed a 15,120 liter UST from Fast Fare in October of 1989. All of the piping systems and USTs had passed the Accutest tightness testing in February of 1990. Two 30,240 liter USTs were removed from Fast Fare on December 29, 1992 (Groundwater Management Associates, Inc., 2005).

A level II Property investigation for the Reade Street parcel was performed by YWC Southeast and the report was submitted on January 9th, 1990, on behalf of Pokegama Inc. The site had previously contained an 1135 liter (300 gallon) UST. Four monitoring wells were installed on the property and soil samples collected. It was determined that the highest

concentration of contaminants was found in the first well (PMW-1) (Figure 3) and the contamination was due to groundwater transport of fuel from the Stop Shop site. However in reviewing the topography of the area, S&ME did not believe that there was movement of contaminants from Stop Shop to Pokegama property (S&ME, 2011). Therefore there was disagreement as to the source of contamination.

Phase V of the investigation began during the week October 29th and November 6th, and nine additional monitoring wells were installed (MW-33-MW-41). The goal of this phase was to determine whether the groundwater located east of Town Creek was contaminated and assess the plumes west of the creek (Groundwater Management Associates, Inc., 2005). There was no free product detected but monitoring wells MW-33, MW-34 and MW-38 showed elevated concentrations of benzene. The report indicated that water quality had improved at the initial seep but hydrocarbon concentrations had increased downstream between the Tar River and First Street. This implied that by spring of 1990, the contaminated groundwater was discharging further downstream along the banks of Town Creek. One of the monitoring wells located east of Town Creek contained contamination on one occasion and another one east of the creek contained trichloroethene and tetrachloroethene. Hydrocarbon odor was detected in the area and a rainbow sheen and iron precipitate was visible in the creek (Groundwater Management Associates, Inc., 2005).

1.7 Proposed Corrective Action for Benzene Contamination

In November of 1991, a Federal Trust Fund contractor Richard Caitlin and Associates submitted an Engineering Report for Proposed Corrective Actions. This report mapped out specification and designs for treatment systems. As part of the treatment system, four wells (RW-1 through RW-4) were installed in the surficial aquifer to facilitate a pump and treat system to

remediate the contamination. As required by the discharge permit, Caitlin submitted the first monitoring report to Greenville Utilities Commission on June 8th, 1992. By May 15th, 1996, there was a cumulative flow of 23,027,382 liters (6,091,900 gallons) that had been pumped and treated. However, the recovery plan was terminated due to Senate Bill 1317, and a request from the Federal Trust to temporarily suspend the cleanup requirement of petroleum from USTs at low priority sites, such as Town Creek. The Washington Regional Office issued a letter to Greenville Utilities Commission on May 1, 1992 that stated, “no responsible parties have been identified besides the current owners of land where contamination exists, which is a long list including the City of Greenville and East Carolina University” (S&ME, 2011). It was hard to pinpoint whom the responsible party for the contamination was even though some hydrogeological evidence had identified five possible sources.

1.8 Town Creek Historic Sampling Scheme and Findings

Due to the suspension of cleaning low priority sites in 1992, it would be many years before Town Creek would be assessed again. A Receptor Survey and Soil and Groundwater Assessment Report on Town Creek was completed in November of 2005 by Groundwater Management Associates, Inc. They reported that on a previous visit, few of the monitoring wells and none of the recovery wells could be found and no water supply wells could be found. Soil samples that were collected near the seep detected petroleum hydrocarbons at concentrations above the State Action Levels. Two monitoring wells (PMW-1 and MW-34) were sampled and in PMW-1 it was detected that concentrations were above the 15A NCAC 2L .0202 ground water quality standard. No constituents were found in MW-34, which was located between the seep and PMW-1 (S&ME, 2011). In addition to soil samples, six surface water samples were also collected SW-1 through SW-6. SW-1 and SW-2 was located upstream and showed no target

constituents. The highest was seen in SW-3, which was located at the seep. Benzene concentrations ranging from 9 to 510 µg/L were found in SW-3 through SW-6, with decreasing concentrations as the water approached the Tar River (S&ME, 2011). In September 2008, Federal Trust Fund contactors, Withers and Ravenel completed the Groundwater, Soil and Surface Water Sampling Report on Town Creek. Monitor well PMW-1 was sampled and benzene were detected above the 2L Standards. In a Groundwater and Surface Water Sampling Report completed by the engineering firm S&ME (2011), it was reported that on December 15, 2010, PMW-1 was sampled and benzene was above the 2L Standards. The water sampled did not exceed the GCLs or surface water quality standards by more than 10 times. The benzene concentration in the water sampled at the seep was 53.4 µg/L compared to 51 µg/L which is the surface water standard (S&ME, 2011).

S&ME attended a meeting on March 23, 2011 at Town Creek with NCDENR representatives. Groundwater upwelling at the seep was observed flowing into the creek, as well as other small seeps along the bank of the creek. The following day, S&ME developed a Proposed Sampling Plan, which was approved by the City of Greenville and NCDENR. Water was sampled according to the plan by S&ME, and afterwards a Surface Water Sampling Report was developed (March 24, 2011). The sampling did not show constituent concentrations above surface water quality standards. A sampling event was scheduled for late August but due to Hurricane Irene it had to be rescheduled and took place on September 16, 2011. Four samples were collected (SW-1, SW-3, SW-5 and SW-6), five seep samples (Seep A1, Seep B1 through B4) and two precipitate samples (PR-1 and PR-2). SW-1 was collected upstream from the seep, SW-3 was collected within the seep area, SW-5 was collected downstream and SW-6 was collected near the Tar River, shown in Figure 3. PR-1 and PR-2 was collected in the same area as

SW-5. During this sampling event, a petroleum odor was apparent, as well as petroleum sheen near the seep (S&ME, 2011).

Following the sampling activity and report, that was completed, it was recommended by S&ME that sampling continue near Town Creek at locations from SW-1, SW-3, SW-4 SW-5, SW-6, Seep-A and Seep-B. This would assist in the monitoring of surface water quality. These samples should be taken quarterly to semi-annual and be scheduled sooner than 3 days following rainfall (S&ME, 2011). The suspected flow of the benzene plume can be seen in Figure 4. The plume appears to me moving in a northeast direction.

1.9 Benzene and Air Quality

Airborne benzene is also hazardous to human and wildlife health. Benzene evaporates into the lower atmosphere quickly from contaminated soil and water and the vapor may sink in low-lying areas. For example strong odors of fuel are often reported by landscaping crews that maintain the grounds along Town Creek and near Town Commons the study site for this research. With warmer weather, people are more likely to spend time in and around this recreational area and may be exposed to contaminated water and air. Therefore, air quality monitoring may also help to protect public and environmental health.

1.10 Fecal Indicator Bacteria and Surface Water Quality

There are a variety of recreational water activities that people partake in at parks near rivers, lakes and streams, especially during the warmer months. As cities urbanize and people leave rural settings, parks serve as a source of recreation and as a means to enjoy nature. The influx of people moving into urban areas leads to more impervious environments, which can increase the amount of storm water runoff. Rain is less likely to infiltrate, percolate and be

filtered in soil, when the land is covered with pavement, roof tops, and hard surfaces. Storm water runoff often transports pathogens, hydrocarbons, sediment, trash and other pollutants to surface water bodies such as rivers and lakes. These pollutants accumulate on impervious surfaces between storms and are “flushed” into receiving waters, thus negatively affecting water quality. For example, polluted storm water runoff is one of the main causes of impairment to almost 40% of the water bodies in the country (Perdek, et. al., 2003). One of the most common pollutants associated with storm water runoff is pathogenic bacteria from animals and human wastes. Pathogens in water can infect humans through ingestion of water or skin contact. When fecal bacteria concentrations in surface waters are continuously elevated, then the water resources may be designated as impaired and placed on the Section 303(d) list of impaired waters via the Clean Water Act (Perdek, et. al., 2003). The US EPA (1986) recommended regulatory thresholds for frequently used fresh water recreational areas are 126 cfu/100 mL for *E. coli* and 33 cfu/100 mL for enterococci. These thresholds were based on geometric means of at least five samples over a 30-day period. The suggested single sample concentrations should not exceed 235 cfu/100 mL (*E. coli*) or 61 cfu/100 mL (enterococci) (US EPA, 1986).

The bacterium *E. coli* lives in human and animal intestines. Most of the *E. coli* strains are harmless and are a very important part of the intestinal tract of humans (CDC, 2015). Some strains such as 0157:H7 have been found to be pathogenic and can cause illnesses such as diarrhea. These strains can be transmitted through consuming contaminated food or water, as well as contact with animals or people (CDC, 2015). This could result in adverse health effects to those exposed. The pathogenic strains of *E. coli* are grouped into pathotypes. The six pathotypes that are associated with diarrhea are referred to as diarrheagenic *E. coli*. The six pathotypes include shiga toxin-producing *E. coli* (STEC) which is most common type, enterotoxigenic *E.*

coli (ETEC), enteropathogenic *E. coli* (EPEC), enteroaggregative *E. coli* (EAEC), enteroinvasive *E. coli* (EIEC), and diffusely adherent *E. coli* (DAEC) (CDC, 2015). In regards to foodborne outbreaks, Shiga toxin-producing *E. coli* is the most common causative agent.

Enterococci are a normal intestinal flora of humans and nearly all animals. They are often found in surface waters and on vegetation. This can occur as a result of contamination by untreated sewage and animal excretion (Huycke, et. al., 1998). There are over 17 different species of enterococci, even though only a few can cause clinical infections in humans (Fraser, 2016). According to the National Nosocomial Infections Surveillance, enterococci are in the top three most common pathogens that can cause nosocomial infections. They have been known to cause bloodstream infections, urinary tract infections (UTIs) and wound infections in hospital settings. These types of infections usually occur in very ill patients (Fraser, 2016). Once inside the body, enterococci can cause serious ailments that are compounded by other health issues, potentially leading to mortality. For example, exposure to the bacteria strain *E. faecalis* has been associated *with* comorbidity factors including “diabetes (36.4%), various types of cancer (30.3%), cirrhosis (6.1%), steroid therapy (19%), antecedent antibiotic treatment (60.6%), and central venous (21.2%), arterial (12.1%), and urinary catheters (63.6%)” (Fraser, 2016). Infections are more common among the elderly and those with weakened immune systems. Infections have been seen to equally distribute between the sexes (Fraser, 2016).

1.11 Bacteria Transport in Urban Runoff

When cities develop and the percentage of impervious surface increases there is often an increase in pollutant transport in streams during storms (Humphrey et al 2015; Bean et al., 2016). Water pollutants such as pathogens can be public and environmental health risks if people consume or recreate in polluted waters. Greenville is an urbanizing city and the average rainfall

during the recreational season (March-September) is approximately 72.90 centimeters while yearly totals are around 126.03 centimeters (U.S. Climate Data, 2015). Prior studies have shown that stream concentrations of fecal indicator bacteria can increase above recommended standards in developing watersheds of the greater Greenville area. For example, a study conducted in two urbanizing watersheds (11% and 30% impervious surface) in Pitt County North Carolina showed an increase in *E. coli* concentrations during storms for both watersheds (Humphrey et. al., 2015). However, the difference in *E. coli* concentrations between base flow and storm flow was more pronounced in the watershed with the higher percentage of impervious surface. The same trend was seen in samples obtained from Green Mills Run, also in Pitt County (Bean et. al., 2016). Samples were collected from Green Mills Run during base flow and storm flow to determine if the concentrations of *E. coli* in the stream were significantly different. The concentrations for base flow samples (geometric mean of 457 MPN/100 mL) were lower relative to storm flow samples (geometric mean of 1979 MPN/100 mL) and the differences were statistically significant at $p < 0.0001$ (Bean et. al., 2016). The Town Creek watershed in Greenville, NC has a high percentage (50%) of impervious surface and receives abundant rain, and thus stream water quality may be degraded via polluted urban runoff. Land use planning to minimize impervious surface area, while maximizing storm water treatment by the use of best management practices such as wetlands and grassy swales may help to reduce runoff and pathogen transport, thus reducing the health risks associated with waterborne illnesses (Mallin, et. al., 2000).

The goal of this study was to determine if the discharge from Town Creek poses a threat to the environment and public health. The specific objectives of the project included: 1) to determine if the benzene concentration in groundwater and surface water exceeded the national standards (51 µg/L); 2) to determine if the air quality standard for benzene was exceeded near

Town Creek (5 ppm for 15 or more minutes); and 3) to determine if the concentrations of *E. coli* and enterococcus exceeded the recreational water quality standards (single sample threshold, 235 cfu/100 mL for *E. coli* and 61 cfu/100 mL for enterococcus).

2. Materials and Methods

2.1 Surface Water Sampling Analysis

Surface water from Town Creek was sampled at least monthly between March and September of 2016 to determine the concentrations of the contaminants *E. coli* and benzene. On a few other occasions water samples were also analyzed for enterococci. The spring and summer are the periods when people are more likely to engage in water-based recreation, and thus this is when exposure to recreational water quality contaminants was likely the highest. This time frame served as the study period. Water samples were collected and environmental readings were recorded at various sampling locations along Town Creek, as shown in Figure 5. The water samples were collected from the creek by hand. Samples were transferred to an YSI 556 calibration cup for various environmental readings including pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential. Stream velocity was measured during each sampling event using a *Global* model FP111 flow meter. The active cross-sectional area of the stream was measured during each event and used along with the velocity data to determine stream discharge. Water samples collected from the stream were placed in the *Hach* 2100P Turbidimeter 46500-00 to determine the turbidity of the water. Water samples were also collected using sterile, labeled bottles and then placed in ice-filled coolers for later analyses in the Environmental Health Sciences Water Lab (*E. coli* and enterococci) or the private lab *Environment 1* (benzene). Samples were analyzed for fecal indicator bacteria concentrations using the IDEXX Enterolert[®] and Colilert[®] media with quanti-tray 2000 methods. Dilution factors of up to 5x were used to help prevent sample numbers from exceeding the maximum values measured on each tray. The media was poured into the sample bottles, mixed thoroughly and dissolved, and then transferred to a labeled IDEXX[®] Quanti-tray. Separate sample bottles

and trays were used for each indicator bacteria. The trays had adhesive backings and contained 49 large and 48 small pockets that held samples of water. After the trays were filled, they were placed into a Quanti-Tray Sealer model 2X IDEXX. This machine sealed the trays by heating the adhesive, concealing the water inside each pocket. The trays were placed in the *Fisher* Isotemp 500 series incubator and heated at 37 degrees (*E. coli*) or 41 degrees (enterococci) for 24 hours before being removed. The incubated trays were placed under a black light (Blak-Ray Lamp model UVL-21) and the wells that illuminated were counted and recorded.

The concentrations of *E. coli* and enterococci were compared to environmental standards established by the US EPA to determine if they pose a threat to the public and environmental health. The *E. coli* and enterococci concentrations in surface water sampling locations including upstream, the seep, across from the seep, and downstream (Figure 5) were compared to determine if statistically significant differences were observed.

Because of funding limitations, one sample was collected once a month for benzene analyses from Town Creek (5 samples) and once from a groundwater well up-gradient from the seep. These samples were collected and sent to Environment 1 for benzene analyses. Sample kits included 6 glass sample bottles and vials of hydrochloric acid. Hydrochloric acid was added to the bottles prior to completely filling them with a water sample. Samples were filled until they exhibited a dome-shape at the top of the bottles to prevent any headspace. Environment 1 used the EPA's Method 602: Purgeable Aromatics to determine benzene concentrations. Method 602 is a method that was approved under the Clean Water Act section 304(h). Under the method it states, "An inert gas is bubbled through a 5 mL water sample contained in a specially-designed purging chamber at ambient temperature. The aromatics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the aromatics

are trapped. After purging is completed, the trap is heated and back-flushed with the inert gas to desorb the aromatics onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the aromatics which are then detected with a photoionization detector” (EPA, 1984).

Benzene mass loading was determined by multiplying the benzene concentration and the discharge of Seep 1 adjacent to Town Creek. The discharge of Seep 1 was calculated by placing a volumetric flask at the base of the seep and measuring the time (via stopwatch) it took to fill the flask. Additional groundwater loading of benzene to Town Creek likely happened along the banks and stream bed on the west side of the creek. With additional monitoring wells along the banks and streambed a better overall estimate of benzene loading could be determined. Environmental readings at Seep 1 were also performed using the YSI 556 MPS and the HACH turbidimeter. Groundwater discharge and environmental readings were also performed at Seep 2 on the opposite side of the creek, but that area was not suspected to be contaminated with benzene.

2.2 Groundwater Sampling Analysis

Water samples were collected from all three existing groundwater wells 7 times during the study for *E. coli* analyses, and once for benzene analyses at groundwater Well 2, closest to Seep 1 (Figure 5). Two wells were located on the east side of Town Creek (Well 1 and 2) and one well was located on the west side (Well 3). The wells were installed to similar depths (12.3-13.9 ft. (374.9-423.7 cm)). A *Solinst* temperature, level and conductivity meter was used to determine the depth to groundwater from each well. Groundwater samples were collected from wells using disposable bailers (new bailer for each well). The wells were purged using the bailers and then samples were collected. The YSI 556 multi-meter was used for determining the physical

and chemical properties of groundwater samples. Groundwater from the three wells was tested for *E. coli* using the same lab procedures as described in the surface water sampling section

2.3 Air Quality Analysis

Benzene exposure can also occur through inhalation, so determining the concentration of benzene in the air was also important for assessing health risks. Soil samples were collected on either side of the creek. One sample location was at Seep 1 and the other was across the creek and upstream from Seep 2. Soil was collected in small zip-lock bags and allowed to sit in the sun. The portable MiniRAE 2000[®] VOC Monitor PGM – 7600 was used to measure the airborne concentrations of benzene in the sample bags (Operation and Maintenance Manual, 2005). The monitor displayed the benzene concentration as ppm. The benzene values for each side of the creek were compared to each other and to the air quality standards (5.0 ppm for a 15-minute time period).

2.4 Statistical Analysis

Benzene concentrations in the water samples were compared to national contact standards (51 µg/L) to determine if the concentrations exceeded the MCL. The frequency of exceedance was reported. Benzene concentrations in the air were also compared to environmental standards. These analyses would help determine if the water and air posed a threat to the environment and public health.

The concentration of bacteria in water samples collected from Town Creek during base flow was compared to concentrations in samples collected during rain events to determine if storm water runoff was influencing water quality. The frequency of MCL violation was reported for base flow and storm flow samples. Statistical comparisons were made using Minitab 17

statistical software. Paired T-tests were used for comparisons when the data showed a normal distribution and Mann Whitney tests were used for data with non-normal distributions.

Comparisons that had p-values of 0.05 or less were considered significant. Bacteria data were graphed using a \log_{10} scale because of the high variability of the data. The physical and chemical parameters of water were summarized for each sampling location, and compared to bacteria and benzene concentrations to determine if obvious relationships existed between the parameters.

3. Results and Discussion

3.1 Benzene Concentrations in Town Creek

One of the objectives of this study was to determine if the benzene discharging into Town Creek exceeded the maximum contaminant level (MCL) and was a public health threat. Prior sampling conducted by the NC DENR for benzene concentrations in the Town Creek Watershed was initiated in November of 2005, and showed contamination was present during that period. The first sample NC DENR analyzed had a benzene concentration of 510 $\mu\text{g/L}$. As shown in Figure 6, there was a sharp decline in the concentrations as more samples were acquired during their study. The final three samples collected by NC DENR had concentrations at or below the national standard for contact (51 $\mu\text{g/L}$). There were sequential samples that fell below the MCL and the water near the seep was not used as a water supply source. The declining concentrations could explain why the site was considered “low risk”. However, since complaints of fuel odors and “sheens” on the water and soil near Town Creek persisted, more monitoring was needed to determine if the threats were still present.

Sampling for this study began in March of 2016. Benzene was detected in all groundwater samples ($n = 5$) collected near the seep. The first sampling event for this study (March 2016) had the lowest concentration (12.55 $\mu\text{g/L}$). It should be noted that due to heavy rain, the Seep 1 area was flooded, possibly diluting the sample with rainwater. The week prior to sampling, there was approximately 12.9 cm of rainfall and the Tar River had risen from 182.9 to 350.5 cm (USGS, 2016). The next sampling two months (April and May), the benzene concentrations increased 2 to 3 times higher than in March. The April and May benzene concentrations were 37.05 $\mu\text{g/L}$, and 31.6 $\mu\text{g/L}$, respectively. During these sampling events, The Tar River had a gauge height of 137.2 cm (April) and 140.2 cm (May). These samples were

collected when water levels were lower, and the Seep 1 area was visible and accessible. The March through May samples had benzene concentrations that were below the national contact standard of 51 µg/L, but higher than the drinking water standard, which is 5 µg/L. The water sampled from the groundwater well (# 1) near Seep 1 had a concentration of benzene (28.7 µg/L) similar to the concentrations near Seep 1 during the first 3 sampling events. The next two sampling events at Seep 1 in late June and early September had the highest concentrations of benzene. The June sample had a concentration of 78.5 µg/L, and the September sample had a concentration of 73.6 µg/L. The stage height of the Tar River during these sampling events was 129.8 cm and 114.6 cm, respectively. Both of these samples had concentrations that were higher than the contact standard of 51 µg/L. These data show that the groundwater discharging into Town Creek from Seep 1 is sometimes higher than the national standards. Two of 5 surface water samples (40%) collected at Seep 1 during this study exceeded the national standards. Seep 1 discharges in Town Creek near the Tar River and the benzene-contaminated discharge has the possibility of negatively affecting those who utilize this area for recreational purposes.

The relationship between the stage height of Tar River at Town Commons and the benzene concentration in Town Creek was evident during the study period. The data showed a trend of increasing benzene concentrations with decreasing stage height of the Tar River. As mentioned previously the lowest concentration of benzene was 12.55 µg/L occurred when the river was at 350.5 cm. The highest concentration of benzene was seen when Tar River was at one of its lowest levels during the study of 129.8 cm. Using the log₁₀ of the stage height and benzene concentration, a linear regression with $R^2 = 0.5802$ was observed (Figure 7).

$$\text{Eq. 1: } y = -0.0052x + 2.4451$$

$$R^2 = 0.5802$$

This equation can be used to predict the concentration of benzene based on the stage height of the Tar River at Town Commons. The stage height of Tar River was not available for the 2005 benzene-sampling event conducted by NCDEQ but other historic sampling events showed that benzene concentration and stage height followed a similar pattern on December 15th 2010 (53.4 ppm; 86.9 cm), May 12th 2011 (33.8 ppm; 137.2 cm) and September 16th 2011 (28 ppm; 160.02). After pooling these data, there was a moderate correlation ($r = -0.675$) between the stage height of the Tar River and the concentration of benzene in Town Commons that was statistically significant at $p = 0.066$. Additional monitoring is suggested to determine if the relationship between the stage height and benzene concentrations persists.

The first sampling period the benzene concentration was 12.55 $\mu\text{g/L}$ and the discharge of the seep was 3.2 mL/ s. Therefore, the mass loading of benzene to Town Creek was determined to be 3.5 mg/day during that sampling event. The highest mass-loading rate recorded occurred during the September sampling event. The benzene concentration was 73.6 $\mu\text{g/L}$ with a discharge of 4.35 mL/s. The benzene-loading rate on this sampling event was 27.7 mg/day. The average mass-loading rate of benzene to Town Creek observed during the study was 16.3 mg/day. At this rate there would be 5.9 g of benzene discharged into Town Creek per year (365 days). The Seep 1 discharge was typically 0.2 to 0.3% of the total discharge of Town Creek.

3.2 Benzene Concentrations in the Air

Soil samples were collected four times during the study from the banks of Town Creek to determine the concentration of benzene released into the air from the soil. Soil samples were collected near the seep and on the opposite side of the creek. The first sampling event took place

on April 5th. The results showed that benzene concentrations in the air near Seep 1 were 4.2 ppm, and were nearly an order of magnitude higher than the concentration of benzene the air on the opposite side of the creek (0.5 ppm) (Figure 8). The next two sampling events took place on April 21st and May 22nd and the samples collected across the creek were just above detection limits of 0.01 ppm. The benzene concentrations in air near Seep 1 measured 51.1 ppm and 28.3 ppm during the same sampling events. The final sampling event occurred on June 29th and the concentration levels were 28.9 ppm near the seep and 5.1 ppm on the opposite side of the creek. These values measured throughout the study were variable but always higher near Seep 1 relative to the other side of the creek. Differences in concentrations were significant at $p = 0.06$.

One of the standards highlighted in the graph is the 50-ppm ceiling and the short-term exposure limit (STEL) according to OSHA's standards. All but one of the samples collected near Seep 1 exceeded OSHA's short-term exposure level of 5 ppm (TOXNET, 2015). The short-term exposure limit is usually 15 minutes. The average concentration of benzene in air near Seep 1 was 28.13 ppm, and the average on the opposite side of the creek was 1.4 ppm. These findings are important because there are many groundskeepers in the area mowing the lawn for extended periods of time. The banks of Town Creek are steep and weed eaters are used to mow the banks. It takes longer than 15 minutes to complete the mowing. There may also be public health threats to the individuals who are employed at the Willis Building or living in First Street Apartments, which is near Town Creek. Various recommended exposure levels for benzene from different administrations can be seen in Table 4. Animal studies supports evidence that benzene increases the risk of adverse health effect. For example, rats exposed to a benzene concentration between 3,526-8,224 ppm for 15 minutes had an increase in the number of ectopic ventricular beats. Other studies showed that rats continuously exposed to 209.7 ppm for a period of 10 days before

breeding showed no signs of pregnancy. Ecotoxicity studies showed that herring larvae exposed to 35-45 ppm of benzene caused a delay in the development of eggs and also produced abnormal larvae (TOXNET, 2015). Repeated exposure at the concentration levels we found during the study could have detrimental health effects on those in the area. Studies have shown that even exposure levels at 1 ppm or less may increase the chances of hematotoxicity (Lan, et. al., 2004). For example, in a study that was conducted on shoemakers in China, 250 workers that were exposed to benzene were compared to 140 workers that were not exposed. The shoemakers had been employed for an average of 6.1 years and each individual's exposure was monitored for 16 months and categorized into groups based on exposure levels. All white blood cell types measured were significantly lower in workers exposed to less than 1 ppm when compared to the controls (Lan et. al., 2004). Based on these findings if the exposure is long enough, concentrations lower than 1 ppm can have detrimental effects on public health.

3.3 Benzene Concentrations in Groundwater

Environmental readings suggest that groundwater near Seep 1 was influenced by the leaking fuel more than groundwater on the east side of the creek near Seep 2 and Well 3. For example, the dissolved oxygen and oxidation-reduction potential readings were significantly ($p < 0.05$) lower in water near Seep 1 (1.65 ± 0.59 mg/L; -217 ± 78) relative to Seep 2 (6.79 ± 1.40 mg/L; -97 ± 63) (Figure 9, Figure 10). The specific conductance and turbidity of water was significantly higher near Seep 1 (431 ± 66 μ S/cm; 206.8 ± 51.5 NTU) in comparison to Seep 2 (230 ± 42 μ S/cm; 12.0 ± 6.0 NTU) (Figure 11, Figure 12). Well-1 and Well-2, which are located on the west side of the creek also had higher specific conductance (549 ± 78 μ S/cm and 457 ± 50 μ S/cm) in comparison to Well-3 (92 ± 20 μ S/cm) (Figure 11). The dissolved oxygen concentration was lower in Well-1 (1.8 ± 1.1 mg/L) and Well-2 (2.8 ± 1.0 mg/L) relative to

Well-3 (3.4 ± 0.9 mg/L) (Figure 9). Prior research has shown that natural biodegradation of benzene in groundwater lowers the redox potential due to depletion of electron acceptors such as oxygen, nitrate, iron, and sulfate (Takahata et al 2006; Gomez et al., 2009). The concentration of reduced iron in groundwater may increase where degradation occurs. When groundwater encounters aerobic environments such as stream beds or seeps, the reduced iron gets oxidized, creating “rust colored” masses as seen near Seep 1 and in Town Creek (Appendix A). The iron masses increased the turbidity of water in Town Creek. These masses were not as prevalent near Seep 2 on the opposite side of Town Creek (Appendix A). The natural attenuation of benzene may be hindered by the accelerated depletion of nutrients and dissolved oxygen, which in turn can increase the lifespan and length of BTEX plumes (Gomez, D., & Alvarez, P., 2009). Prior studies have also shown that the amount of dissolved oxygen and oxidation-reduction potential both decreases with the presence of BTEX compounds in groundwater (Takahata et al 2006). Comparing environmental readings in the monitoring wells and seeps on the west to the east side of the creek shows the influence that the leaking fuel is having on the groundwater. Overall, these data suggest that benzene concentrations are higher in groundwater on the west side of the creek.

3.31 Base Flow vs. Storm Flow Environmental Parameters

There were many distinctions that were observed in surface water following periods of rainfall. During storm events, there were increases in water flow, turbidity, oxidation-reduction potential and temperature of surface waters (Table 3). The differences in stream discharge between base flow and storm flow were significant at $p = 0.002$. On average, the measured discharge during base flow was (5.4 ± 2.8 L/s) and storm flow was (28.8 ± 5.7 L/s). Stream turbidity followed a similar pattern of increasing during storm flow. The average turbidity during

base flow was 10.7 ± 12.4 NTU while the average turbidity during storm flow (169.3 ± 56.9 NTU) was significantly $p = 0.007$ higher. This could be explained by the increase of sediment in surface water during storm flow compared to base flow. Another environmental parameter that changed between the two sampling events was the oxidation-reduction potential (ORP) in water. The average ORP during base flow was $(-148 \pm 20 \text{ mV})$ while the storm flow average was $(-44 \pm 65 \text{ mV})$. The differences in oxidation-reduction potential were significant at $p=0.002$. These differences were likely influenced by oxygenated runoff from storm water, in relation to the percentage of flow that is ground water.

3.32 – Base Flow and Storm Flow Fecal Indicator Bacteria Concentrations

To determine the impact that storm water runoff had on the microbial water quality of Town Creek, water samples were collected during 4 base flow and 4 storm flow events and compared. The bacteria concentrations increased during each storm flow relative to base flow conditions (Figure 13). For example during the July sampling event, base flow *E. coli* concentration was 480 MPN/100 mL, while the storm flow *E. coli* concentration was 1,248 MPN/100 mL. The second sampling event during early September had a base flow concentration of *E. coli* of 37 MPN/100 mL, while the storm flow concentration was 837 MPN/100mL. Later in the same month, the base flow *E. coli* concentration was 53 MPN/100mL and the storm flow concentration was 127 MPN/100 mL. Finally, in October the base flow concentration was 26 MPN/100 mL and during rainfall it increased to 467 MPN/100 mL. Therefore for every sampling event, the storm flow concentration of *E. coli* was elevated relative to the base flow concentration. The differences in the concentrations of bacteria during base flow and storm flow were significant with a p-value of 0.05. Similar trends were observed with the indicator bacteria enterococci. Specifically, the geometric mean of enterococci for two summer base flow events

was 52 MPN/100 mL while the geometric mean during two summer storms was 1194 MPN/100 mL. The results of this study proved that there was a significant increase in the number of the fecal indicator bacteria in Town Creek during storm events relative to base flow conditions. With the high percentage (50%) of impervious surface in the area, storm water runoff contributes to the increase in pathogens in Town Creek. Other research (Humphrey et al., 2015; Bean et al., 2016) conducted in the area has also shown this pattern.

Various water quality parameters like high nutrient levels and turbidity have been reported to help prolong survival of pathogenic bacteria (McLellan, et. al., 2007). During this study a relationship between *E. coli* concentrations and water temperature was observed. More specifically, at temperatures above 18⁰ C, *E. coli* concentrations were significantly higher ($p \leq 0.05$) than levels below 18⁰ C. The average concentration of *E. coli* below 18⁰ C was 18 MPN/100 mL. This was significantly lower than the average concentration of 1455 MPN/100 mL seen with temperatures above 18⁰ C. With warmer temperatures, bacteria tend to grow quicker, and animals appear to be more active, contributing more waste to waterways (Bean, et. al., 2016).

3.33 Fecal Indicator Bacteria and Groundwater

Groundwater was also analyzed for bacteria concentrations. Water samples were collected from three groundwater wells (Well-1, Well-2 and Well-3) near Town Creek. Well-1 and Well-2 were located on the same side of the creek as Seep 1, which was contaminated with benzene (west side), while Well-3 was located on the opposite side of the creek (east side) (Figure 5). The results show that the concentrations of *E. coli* were greater in Well-1 and Well-2 when compared to Well-3. The geometric mean concentration was 255 MPN/100 mL and 453

MPN/100 mL for Well-1 and Well-2, respectively. Well-3, which had lower concentrations throughout the study, had a geometric mean concentration of 134 MPN/100 mL (Table 2). Although there were higher concentrations in Well-1 in comparison to Well-3, the differences were not significant. Comparison of bacteria concentrations between Well-2 and Well-3 however showed a significant difference with a p-value of 0.05. The *E. coli* and enterococci concentrations near Seep 1 were higher than near Seep 2 on 67% of the sampling dates, but the differences in median concentrations were not statistically significant. Research has shown that benzene can be lethal to *E. coli* at concentrations of 0.5 ppm (Berno et al., 2004). The benzene concentrations at Seep 1 and Well 1 were typically an order of magnitude lower than that threshold during this study, and thus may not have had much of an influence on *E. coli* concentrations.

Groundwater in Well-2 had an average temperature of $18.6 \pm 2.2^{\circ} \text{C}$ and *E. coli* with a geometric mean concentration of 229 MPN/100 mL. These data were higher in comparison to Well-1 and Well-3, which had average temperatures of $(17.9 \pm 1.9^{\circ} \text{C})$ and $(16.6 \pm 1.2^{\circ} \text{C})$ and geometric mean concentrations of *E. coli* that were 50 and 16 MPN/100 mL, respectively.

4. Conclusions

The goal of this study was to determine if the discharge from Town Creek poses an environmental and public health risk. Workers in the Town Creek area reported the smell of fuel and the Greenville Fire Department identified a seep that contaminated with gasoline at the bottom of a ravine near Town Creek in the 1980's. This discovery prompted the North Carolina Department of Environmental and Natural Resources to open an investigation (Groundwater Management Associates, Inc., 2005). Some remediation steps including removal of underground tanks, and pumping and treating of contaminated groundwater were undertaken to improve water quality. However, after 30 years, groundwater contaminated with fuel continues to discharge into Town Creek. Town Creek is also influenced by storm water runoff from impervious surfaces in the watershed. Urban runoff can transport various pathogens to the Town Creek. Town Creek discharges into the Tar River, which is adjacent to Town Commons, an area that is promoted by the city as a local recreational attraction. As water from Town Creek empties into the Tar River, patrons may be exposed to bacteria and fuel products, which in turn can have negative effects on their health. So two important questions addressed during this study were 1) are benzene concentrations in water and air near the creek in high enough concentrations to pose a threat to public health; and 2) are the concentrations of indicator bacteria present in the creek elevated relative to state and federal standards?

Results from this study showed that the water and air near Town Creek does have the potential to exceed national standards in regards to benzene concentrations. Forty percent of the surface water samples collected at a seep along the banks of Town Creek had benzene concentrations that were over the water quality standard of 51 µg/L. The air quality standards were violated even more frequently. Concentrations higher than standards could possibly place

the public in risk of experiencing adverse health effects due to over exposure from the hydrocarbon. Previous monitoring in the area conducted by the Department of Environmental and Natural Resources indicated that the benzene concentrations in groundwater were below national standards and thus sampling ended. This research has shown that there are periods when the benzene concentrations do exceed the national standards.

Due to limited funding, benzene concentrations in surface waters were sampled 5 times during this study, and groundwater was sampled once. More sampling is suggested to gain a better understanding of the temporal variability of benzene concentrations near the seep. Town Creek is in close proximity to Town Commons and with continuous complaints from people in the area, more research is needed to determine the potential public and environmental health threat associated with discharge from the creek. Analyzing the benzene concentration in the soil and air is suggested in addition to water quality sampling. Installing additional monitoring wells in the parking lot up-gradient from the seep could also help determine the extent of the contamination. If there were more ground wells in the parking lot they could be sampled for benzene and this could better pinpoint the direction of the contaminant flow. The monitoring wells installed by NCDEQ were either abandoned or not found in the files that were provided to Groundwater Management Associates, Inc., so determining the source of the contamination could help speed up the remediation process.

Fecal indicator bacteria such as *E. coli* and enterococci can be used to assess the potential for public health threats associated with the presence of pathogens in surface waters. These indicators are used because they have shown a strong correlation with outbreaks of many diseases when their concentrations exceed certain thresholds. These bacteria are present in the gastrointestinal tract of most warm-blooded animals (McLellan, et. al., 2007). Many pathogens

live in gastrointestinal tracts of warm-blooded animals and can be excreted with feces onto land surface. The feces can be transported to surface waters during storm events and potentially contribute to water quality degradation (US EPA, 2003). A study that included analysis of land use and demographic factors showed that fecal coliform abundance was correlated with the percentage of developed land within the watershed and the watershed population (Mallin, et. al., 2000). In this current study, data indicated that greater than 40% of samples collected exceeded the standard during base flow. Storm flow typically contained higher concentrations of indicator bacteria and 75% of the samples collected during storm flow were over the standards for bacteria in recreational waters. When pathogenic bacteria concentration exceeds the national standard, the chances of someone becoming ill from the exposure increases. As noted previously pathogenic bacteria such as *E. coli* and enterococcus can lead to a variety of gastrointestinal disorders. The source of these pathogenic bacteria can come from a variety of sources such as waste products from pets, humans, waste water and wildlife creatures.

The City of Greenville and East Carolina University have received grants to install storm water control measures within the Town Creek watershed and monitor the water quality of Town Creek before and after the implementation of the measures. One of the control measures includes planting trees along the banks of Town Creek near Seep 1. These measures will hopefully help improve the water quality of Town Creek and thereby reduce the public and environmental health risks associated with the discharge from the creek.

5. Tables

Table 1. State of North Carolina Backlog of Leaking Underground Storage Tanks. (EPA, 2011)
Asheville (ASH), Fayetteville (FAY), Morrisville (MOR), Raleigh (RAL), Washington (WAS),
Wilmington (WIL), Winston-Salem (WS)

	ASH	FAY	MOR	RAL	WAS	WIL	WS
State Backlog Contribution	10%	11%	18%	20%	11%	9%	21%
Historical Releases	1,824	1,359	3,394	2,941	1,649	1,275	3,404
Open Releases	649	675	1,153	1,253	691	545	1,377
Closed Releases	1,175	684	2,241	1,688	958	730	2,027
Contaminated Media							
Groundwater	403	536	796	853	656	447	928
Soil	246	137	349	332	35	93	424
Unknown	-----	2	8	68	-----	5	25

Table 2. *E. coli* concentrations in groundwater monitoring wells near Town Creek. Wells 1 and 2 were on the east side of the creek and Well 3 was on the west side of the creek.

	Well 1	Well 2	Well 3
4/5/16	1 MPN/100 mL	133 MPN/100 mL	1 MPN/100 mL
4/21/16	1 MPN/100 mL	15 MPN/100 mL	21 MPN/100 mL
5/11/16	480 MPN/100 mL	783 MPN/100 mL	783 MPN/100 mL
5/22/16	73 MPN/100 mL	995 MPN/100 mL	5 MPN/100 mL
6/15/16	904 MPN/100 mL	816 MPN/100 mL	15 MPN/100 mL
7/26/17	105 MPN/100 mL	72 MPN/100 mL	1 MPN/100 mL
9/1/16	224 MPN/100 mL	358 MPN/100 mL	15 MPN/100 mL

Table 3. Average and standard deviation of environmental readings including specific conductivity (SC), dissolved oxygen (DO), pH, temperature, oxidation reduction potential (ORP), turbidity, E. coli, enterococcus.

Sampling Location	SC (µS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Turbidity (NTU)	E. coli (MPN/100 mL)	Enterococcus (MPN/100mL)
Upstream	339 (42)	11.0 (1.1)	7.19 (0.32)	19.4 (3.1)	86 (54)	5.8 (4.5)	104 (599)	137 (136)
Seep 1	378 (119)	3.1 (3.2)	6.55 (0.48)	21.0 (4.0)	193 (90)	175.8 (97.9)	393 (539)	374 (458)
Seep 2	230 (42)	6.8 (1.4)	6.48 (0.17)	18.5 (3.2)	97 (63)	12.0 (6.0)	760 (712)	445 (589)
Downstream	253 (111)	6.0 (0.7)	6.61 (0.13)	16.9 (1.9)	87 (57)	24.5 (11.9)	73 (250)	108 (229)
Well 1	549 (78)	1.8 (1.1)	6.56 (0.28)	17.9 (1.9)	122 (35)		50 (331)	
Well 2	457 (50)	2.8 (1.0)	6.35 (0.20)	18.6 (2.2)	104 (27)		229 (405)	
Well 3	92 (20)	3.4 (0.9)	6.36 (0.44)	16.6 (1.2)	21 (16)		16 (315)	

Table 4. Recommended exposure levels for various types of benzene exposure. (TOXNET, 2015).

Type of Exposure	Standards	Time Duration
Human (Inhalation)	25 ppm 50 ppm 5 ppm	Ceiling *not to be exceeded more than 10 minutes TWA – 15 minutes
Human (Skin Contact)	51 µg/L	*not to be exceeded
Human (Drinking)	10 µg/L	*not to be exceeded
Rat (Spargue-Dawley)	13,700 ppm (LC 50)	4 hours
Rabbit	45,000 ppm	3.7-36.2 minutes (death at 36.2 ppm)

6. Figures

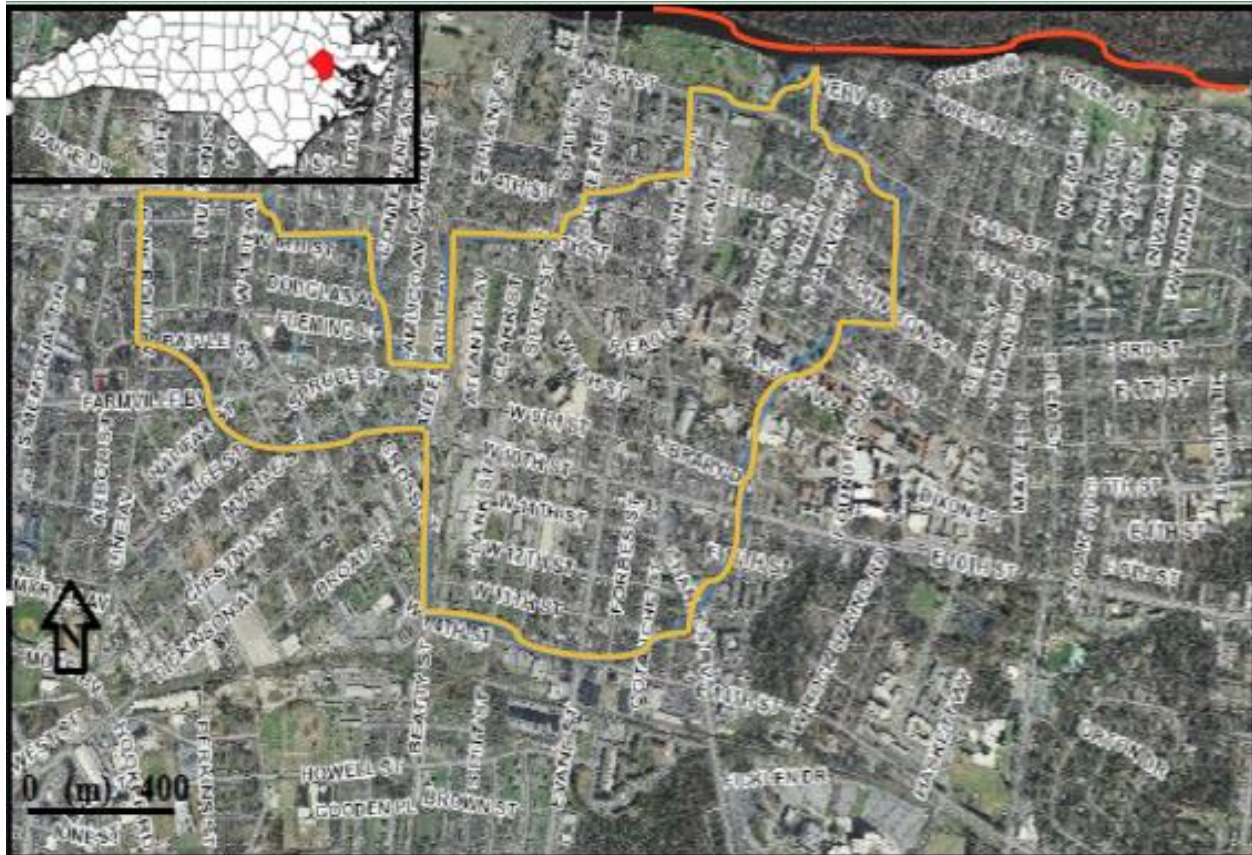


Figure 1. Town Creek in Pitt County, Greenville, NC. The watershed area is shown in a yellow outline. The Tar River shown as red line.

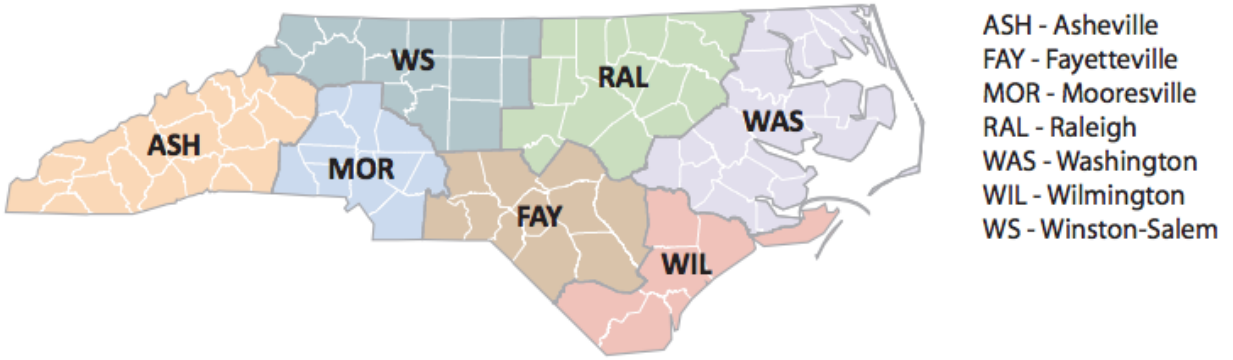


Figure 2. Map of DENR Regions. Retrieved from “The National LUST Cleanup Backlog: A Study of Opportunities”. EPA. (2011)

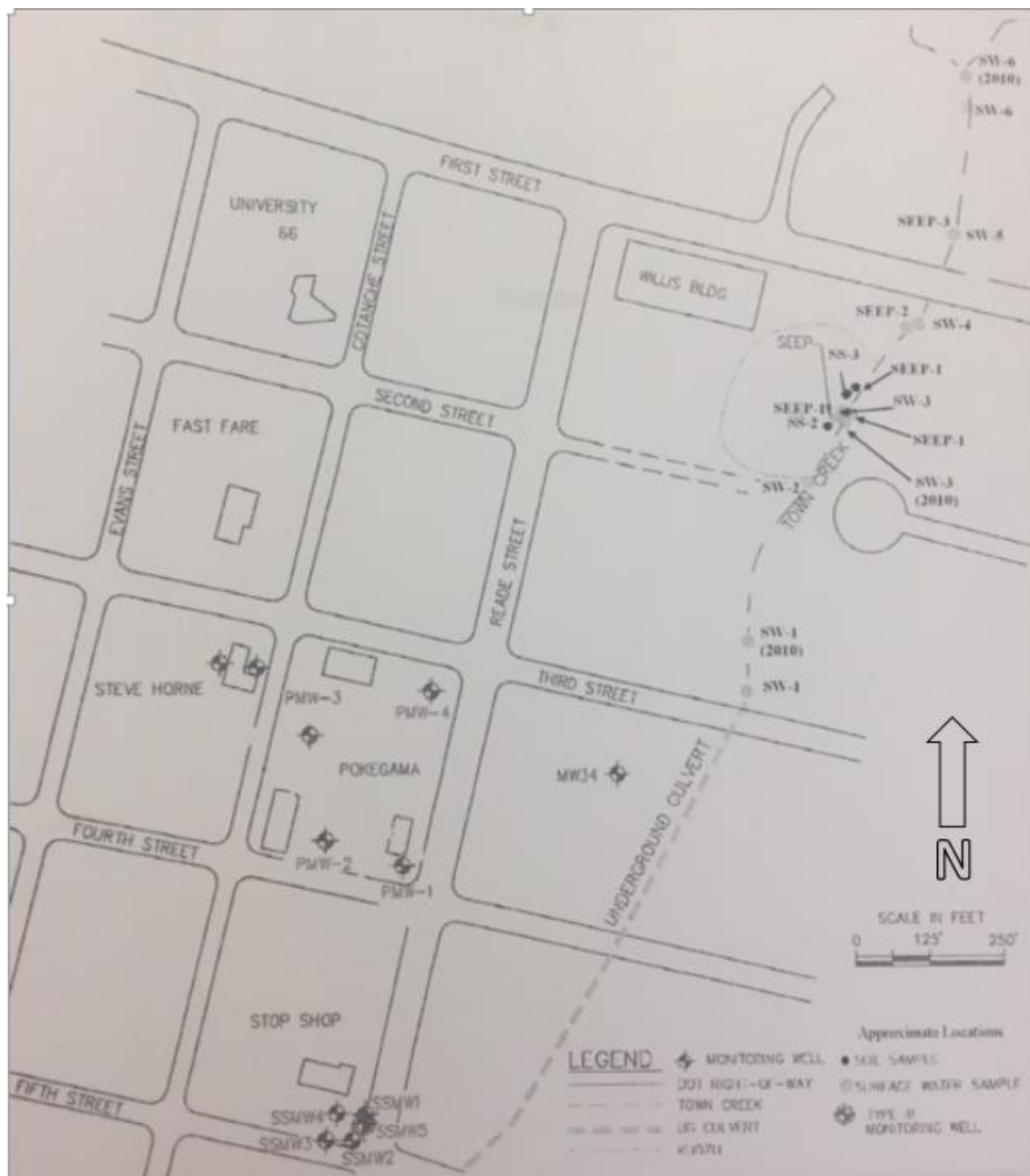


Figure 3. NC DENR benzene sampling locations in Town Creek watershed (S&ME, 2011).



Figure 4. Suspected benzene contaminated groundwater plume (NC DENR, 1990).



Figure 5. Water sampling locations used by ECU researchers in the Town Creek watershed.

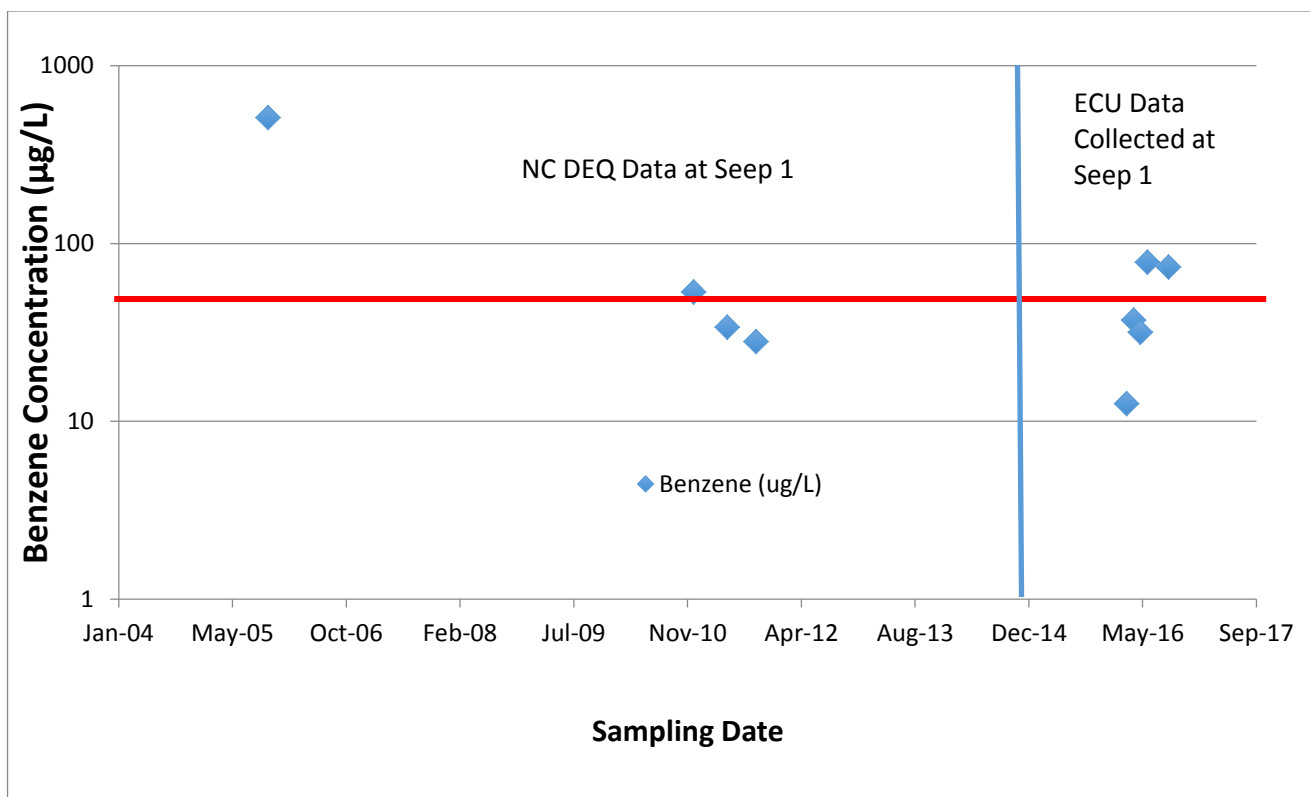


Figure 6. Benzene concentrations in water samples collected near Seep 1 along the banks of Town Creek between 2004 and 2016. Sampling for this study began in 2016, prior sampling was conducted by NC DEQ and engineering firms.

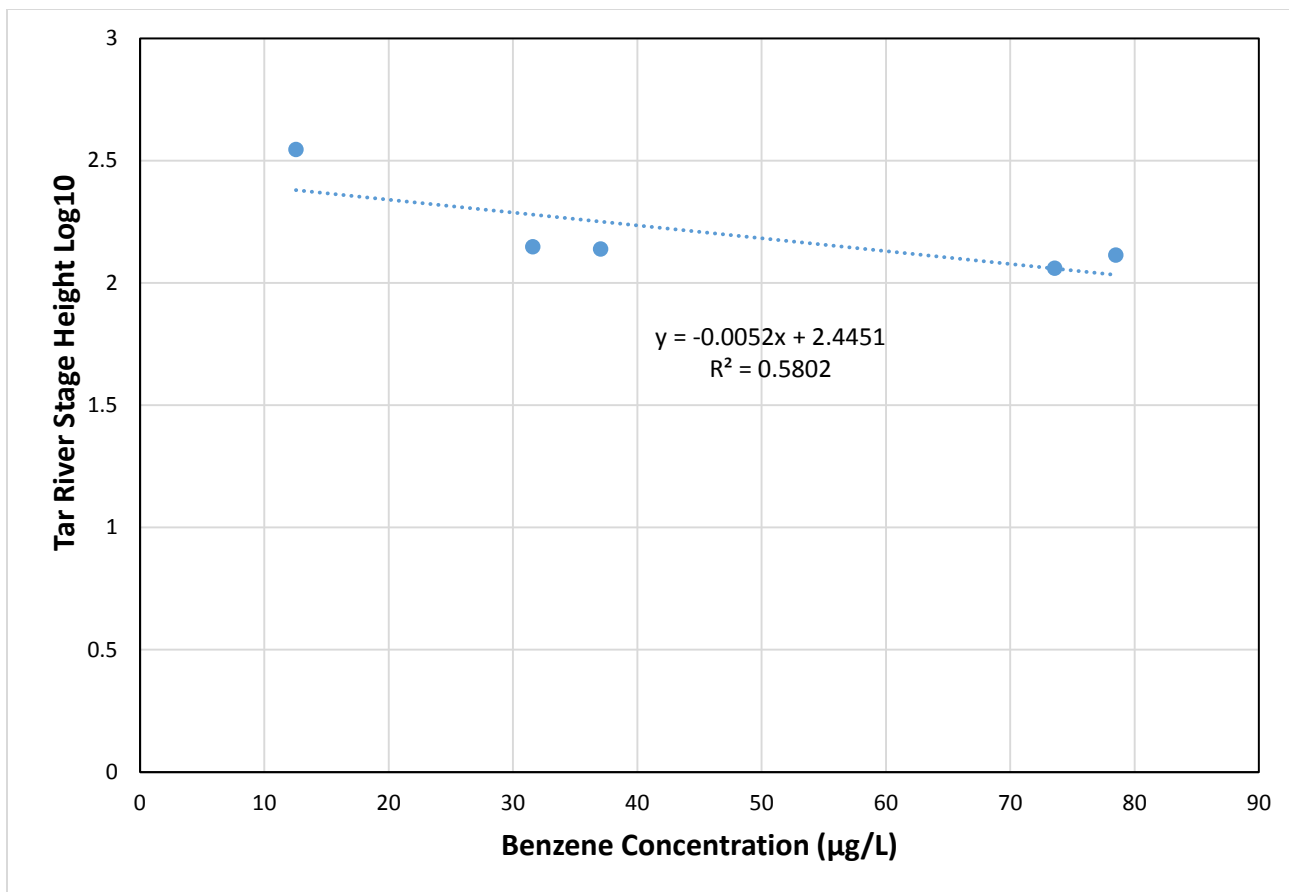


Figure 7. Tar River stage height (Log10 of cm) and benzene concentrations at Seep 1.

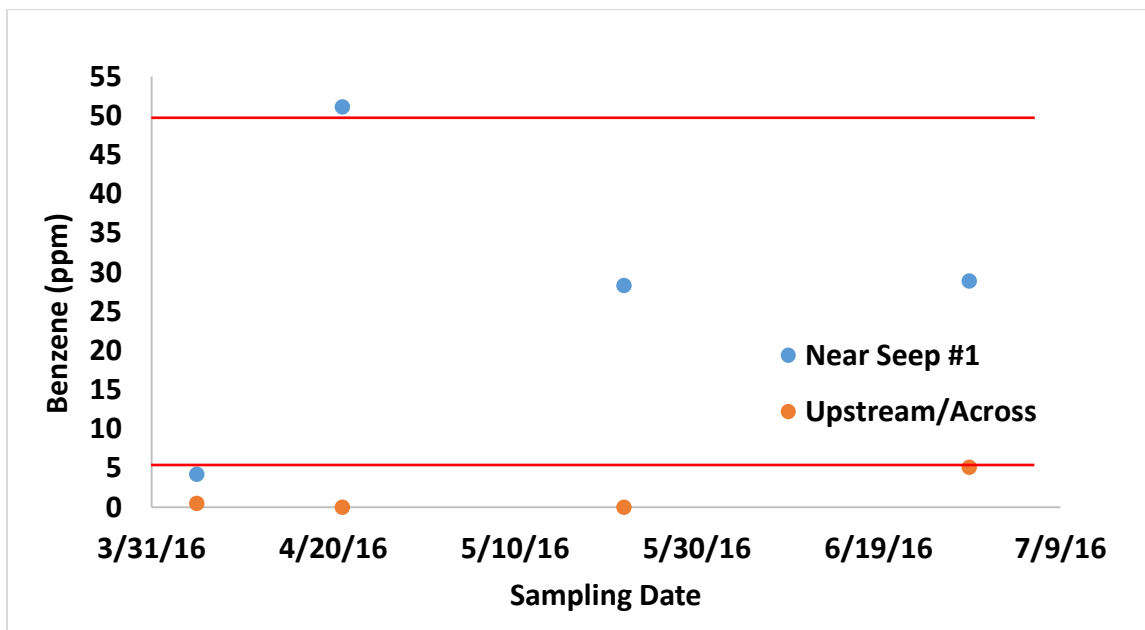


Figure 8. Benzene concentrations emitted into the air from soil samples collected near Seep 1 and on the opposite side (East) of Town Creek.

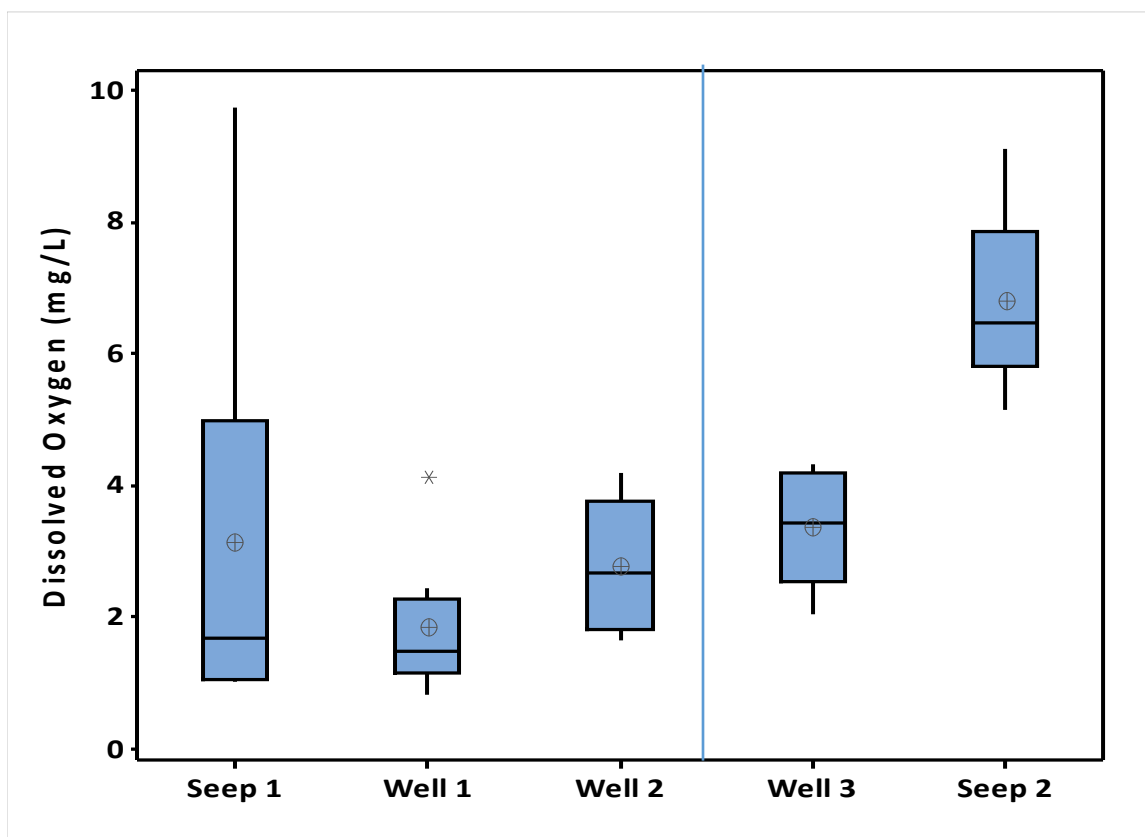


Figure 9. Comparison of dissolved oxygen concentrations in sampling locations on the east and west banks of Town Creek.

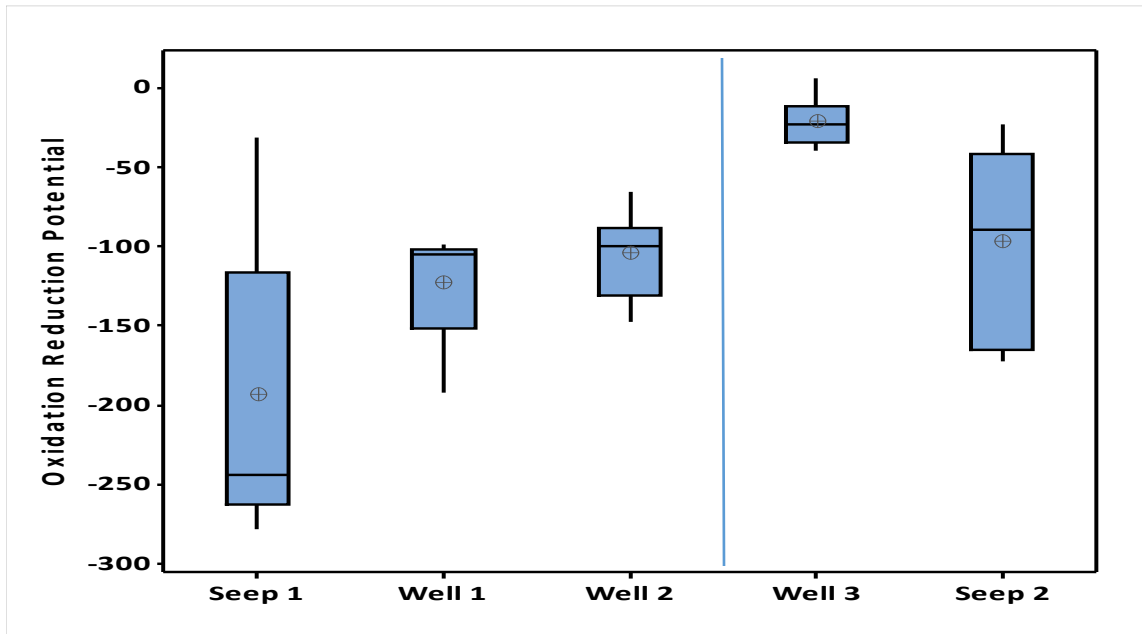


Figure 10. Oxidation-reduction potential in sampling locations on the east and west banks of Town Creek.

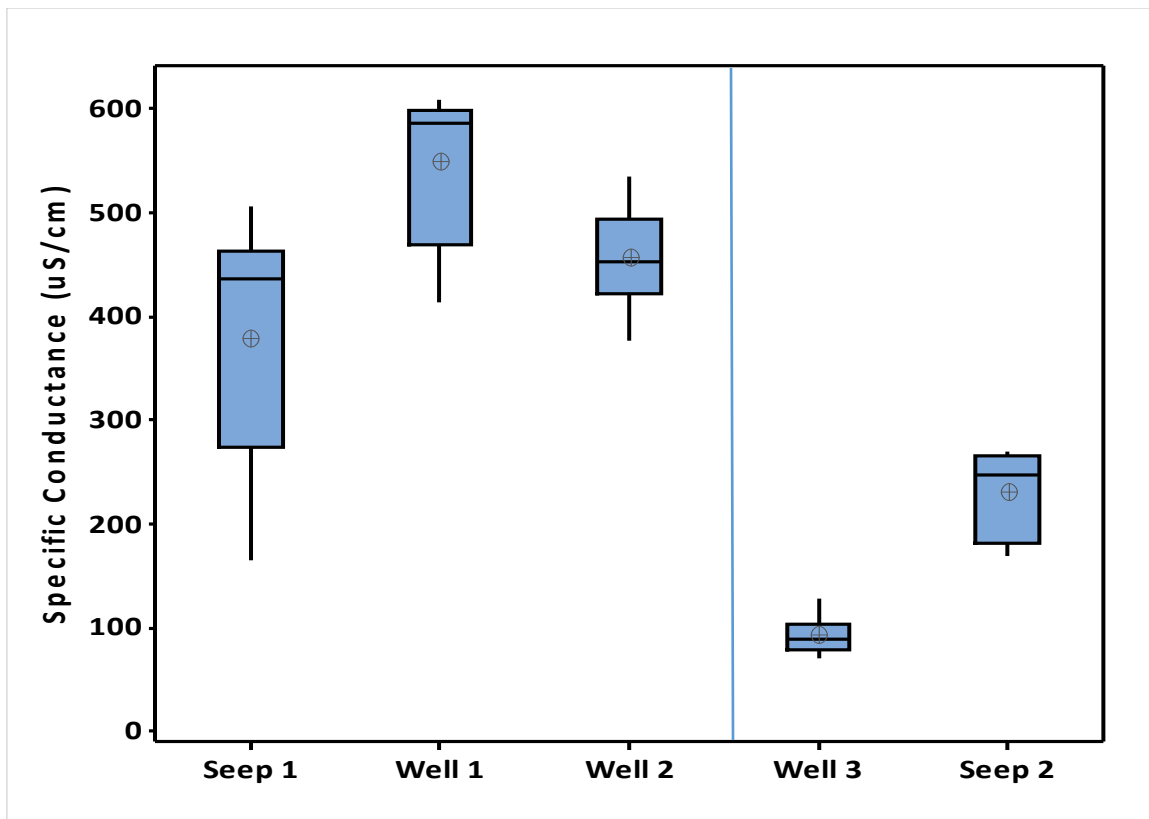


Figure 11. Specific conductance of water at sampling locations on the east and west banks of Town Creek.

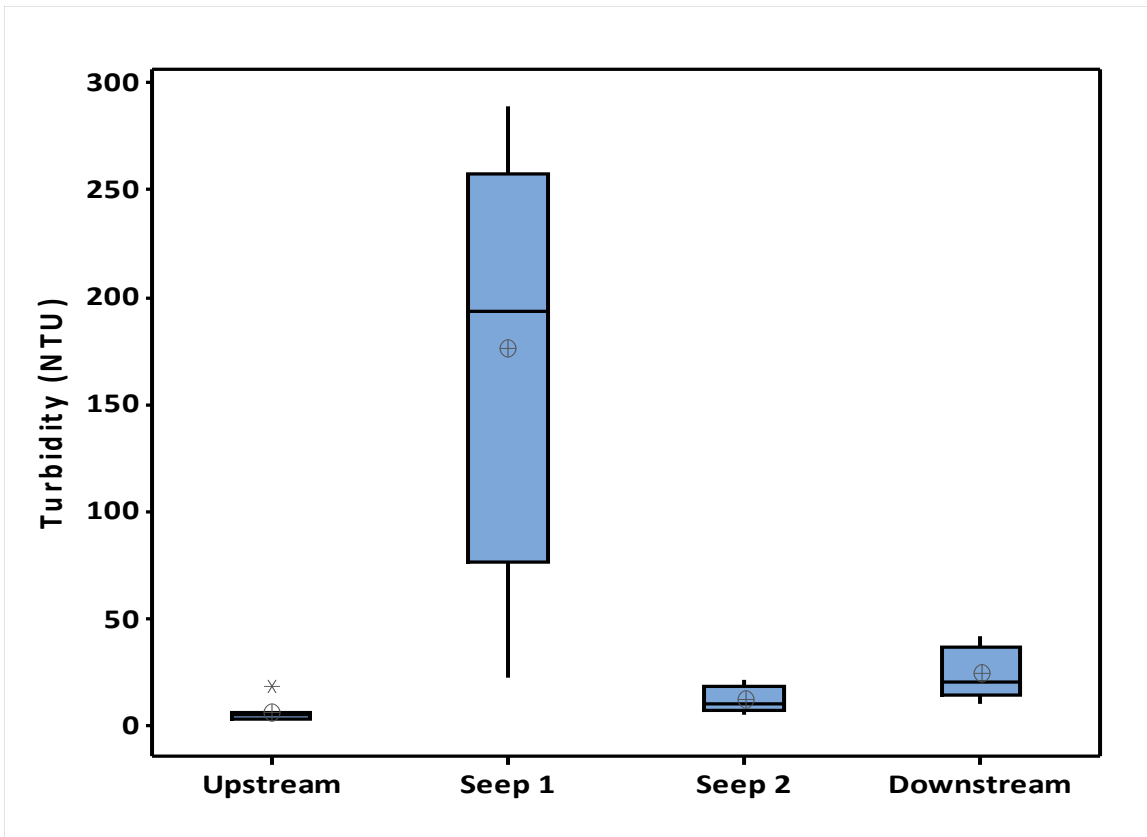


Figure 12. Comparison of turbidity in surface water sampling locations moving from upstream towards downstream.

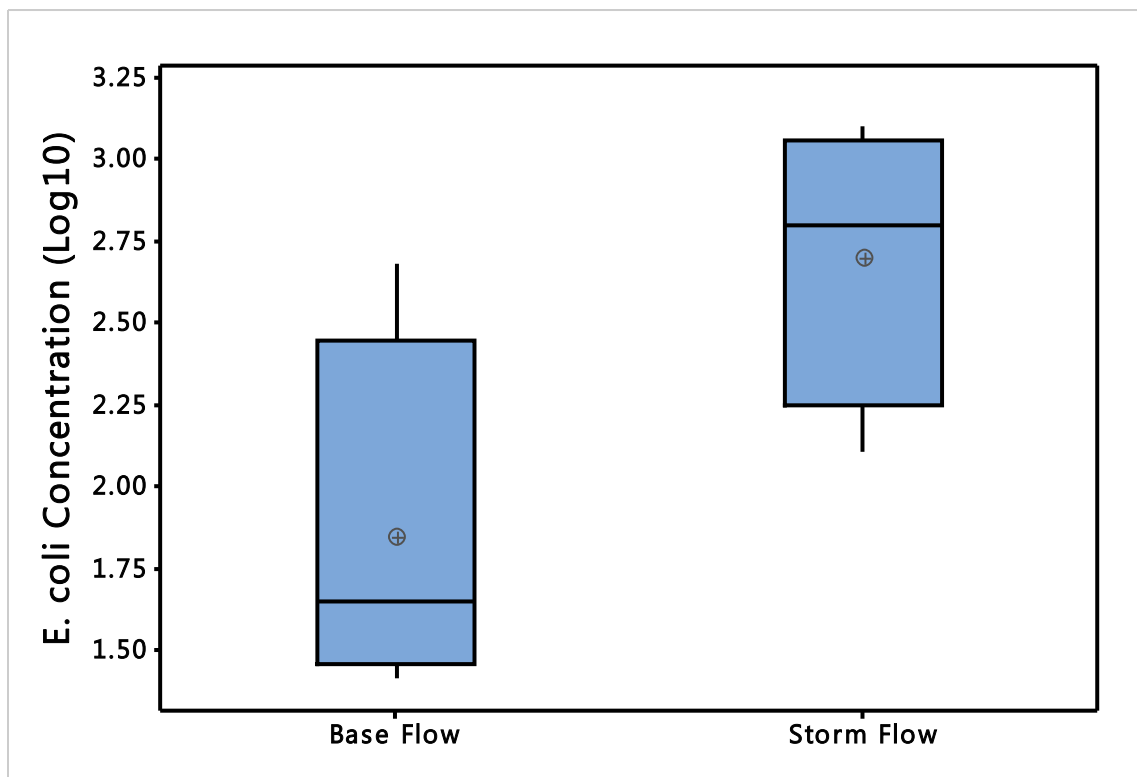


Figure 13. Comparison of the log10 of MPN *E. coli* concentrations in Town Creek during base flow and storm flow.

7. References

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APPENDIX A – SITE PICTURES

Town Creek – Upstream

June 29th 2016



Groundwater sampling near Town Creek

April 5th 2016



Town Creek – Near Seep1

April 5th 2016



Town Creek – Near Seep1

April 21st 2016



Oily Sheen Found at Seep 1

April 5th 2016



Groundwater Seeping into Town Creek

April 5th 2016



Ducks on the bank of Town Creek near Seep 1

April 5th 2016



Duck eggs found on banks of Town Creek

June 14th 2016



APPENDIX B- ENVIRONMENTAL READINGS

Seep 1

Date	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Turbidity (NTU)	E. coli (MPN/100 mL)	Enterococcus (MPN/100mL)
3/21/16	437	1.05	6.53	14.48	-155	289	12	195
4/5/16	506	1.03	6.73	16.9	-244	221	21	10
4/21/16	465	1.09	6.56	17.3	-175	187	670	30
5/11/16	166	9.75	6.36	22.07	-31.2	23	776	1,141
5/22/16	450	1.7	6.27	22.82	-77	247	995	144
6/15/16	460	2.25	6.37	21.4	-278	269	904	725
6/29/16	331	1.37	6.01	24.56	-270	194	1,715	
7/19/16	217	7.55	7.71	26.93	-253	29.1	904	
9/1/16	371	2.43	6.42	22.4	-256	123	1,223	

Seep 2

Date	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Turbidity (NTU)	E. coli (MPN/100 mL)	Enterococcus (MPN/100mL)
3/21/16								
4/5/16	270	6.94	6.65	14.36	-172.4	5	1,663	
4/21/16	264	6.02	6.61	16.4	-162.3	12	1937	1124
5/22/16	247	6.03	6.53	17.03	-23.1	8	265	73
6/15/16	246	5.15	6.33	19.86	-47	9	260	138
6/29/16	170	9.12	6.56	19.88	-61	17	1223	
9/1/16	185	7.45	6.23	23.43	-117	21	712	

Upstream

Date	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Turbidity (NTU)	E. coli (MPN/100 mL)	Enterococcus (MPN/100mL)
3/21/16	349	10.97	7.07	14.68	-120	5	6	19
4/5/16	368	11.5	7.17	16.61	-121	5	10	195
4/21/16	368	11.86	7.3	17.19	32	2.7	26	10
5/11/16	338	10.46	7.51	22.06	-21.8	5	1,547	394
5/22/16	345	10.4	6.47	19.1	-48	18	1,455	101
6/15/16	378	12.3	7.24	17.9	-118	3	467	189
6/29/16	230	8.65	7.1	17.51	-124	6	94	52
	326	11.92	7.61	23.25	-112	2.52	480	
	335	12.13	7.41	23.43	-119	7	37	
	354	10.23	7.03	22.34	-109	4	53	

Storm water samples

	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Turbidity (NTU)	E. coli (MPN/100 mL)	Enterococcus (MPN/100mL)
Before Rain								
7/19/16	326	11.92	7.61	23.25	-112	2.52	480	
After Rain								
7/19/16	155	5.76	7.57	25.46	14	176	1247.5	2306
Before Rain								
9/1/16	335	12.13	7.41	23.43	-119	7	36.5	52
After Rain								
9/1/16	278	6.23	7.37	24.62	-21	122	837	618
Before Rain								
9/18/16	354	10.23	7.03	22.34	-109	4	53	
After Rain								
9/18/16	176	6.43	7.02	23.21	-32	132	127	
Before Rain								
10/13/16	217	7.55	7.71	26.93	-253	29.1	904	
After Rain								
10/13/16	240	7.75	7.89	27.02	-137	247	1718	1252

Downstream

Date	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Turbidity (NTU)	E. coli (MPN/100 mL)	Enterococcus (MPN/100mL)
3/21/16	175	5.25	6.57	16.25	-110	14	563.5	47
4/5/16	414	6.24	6.6	15.53	-156	17	531	1
4/21/16	141	6.11	6.78	15.33	-143	22	480	5
5/11/16	141	6.21	6.55	15.89	10.7	19	1	573
5/22/16	238	5.42	6.45	16.75	-42.1	10	21	16
6/15/16	418	4.91	6.8	17.37	-113	35	143	5
6/29/16	281	7.18	6.68	16.4	-41	37	32	
9/1/16	212	6.45	6.45	21.35	-98	42	59	

Well #1

Date	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Depth (ft)
3/21/16	585	1.18	6.7	17.29	-164	10.35
4/5/16	609	1.2	6.88	16.1	-192	10.58
4/21/16	588	0.83	6.41	16.61	-102	10.74
5/11/16	570	1.88	6.09	21.18	-102.9	10.6
5/22/16	587	1.15	6.34	16.3	-101.3	10.61
6/15/16	603	1.8	6.4	20.2	-106.5	10.77
7/26/16	415	4.12	6.84	17.5	-113	8.3
9/1/16	435	2.43	6.78	17.82	-98.2	9.5

Well #2 (pungent odor)	SC (μS/cm)	DO (mg/L)	pH	Temp (° C)	ORP (mV)	Depth (ft)
3/21/2016	436	3.01	6.4	17.8	-147.6	6.9
4/5/16	376	4.2	6.46	16.4	-139	8.1
4/21/16	418	2.48	6.11	16.2	-65.7	8.31
5/11/16	453	1.67	6.13	20.73	-90.6	6.9
5/22/16	486	1.8	6.19	21.54	-87	8.18
6/15/16	454	1.9	6.39	20.9	-102	8.76
7/26/16	536	4.04	6.4	17.2	-104.5	9.75
9/1/16	498	2.89	6.7	17.76	-98.3	9.8
Well #3						
4/21/16	129	3.1	5.8	16.4	6.3	8.15
5/11/16	70	2.73	6.9	19.02	-33.2	8.25
5/22/16	87	4.16	6.69	16.1	-39	8.02
6/15/16	91	2.04	6.52	16.16	-16.7	8.33
7/26/16	82	4.33	5.9	15.8	-23.4	8.21
9/1/16	94	3.78	6.34	16.2	-22.3	8.35

APPENDIX C- SAMPLING DATE AND BENZENE CONCENTRATION LEVEL AT SEEP-1

Sampling Date	Benzene Concentration
3/21/16	12.55 µg/L
4/21/16	37.05 µg/L
5/22/16	31.6 µg/L
6/15/16	78.5 µg/L
9/1/16	73.6 µg/L

APPENDIX D- GROUNDWATER AND SURFACE WATER SAMPLING LOCATION
COORDINATES IN TOWN CREEK

Sampling Location	Sampling Coordinates
Seep-1	35° 36' 49.7808" N 77° 22' 6.3984" W
Seep-2	35° 36' 49.806" N 77° 22' 6.2184" W
Well 1	35° 36' 46.5372" N 77° 22' 8.8068" W
Well 2	35° 36' 49.734" N 77° 22' 6.6432" W
Well 3	35° 36' 47.6784" N 77° 22' 7.6764" W
Upstream	35° 36' 48.1356" N 77° 22' 7.698" W
Downstream	35° 36' 51.0372" N 77° 22' 5.6964" W