1. INTRODUCTION AND PURPOSE

The process of urbanization results in changes to topography, surface and subsurface geologic conditions and changes the fluxes of atmospheric, hydrologic, anthropogenic, and geologic sourced materials (nutrients, pollutants) within a watershed system. In the earth's system, water is a universal medium because of its abundance in both living and nonliving parts of the system, its role as the universal solvent and its mobility. Thus, the process of urbanization has a direct impact on the physical, chemical, radiological and biological makeup of water.

Through engineering and technological advancements over time, the industrial cities which were originally plagued with pollution and water borne diseases, transitioned into sanitary cities, in which the local government and municipalities took on the role of planning and infrastructure development. But, as the urban population increases and infrastructure ages, the stress on the environment is increasing. The direct implication of this effect is visible in the expansion of urban infrastructure in the suburban areas around cities which contributes to urban sprawl. The increasing realization of the stress caused by urbanization and the limiting buffering capacity of the environment has led to the development of sustainability science. Sustainability science focuses on transdisciplinary approaches to solving problems related to newly developing environmental challenges (Childers et al. 2014). This approach builds on the transcending interactions of the biophysical and socio-cultural components and the sustainability of ecological services. Thus, in the pursuit of moving water quality in urban areas from sanitary to sustainable (Kaushal & Belt, 2012; Pincetl, 2010) various methods and tools have been developed. For example, stream restoration, stormwater management - best management practices (BMPs), green infrastructure (GI) and low impact development (LID), Stormwater Green Infrastructure (SGI) (Gagrani et al. 2014; O'Driscoll et al. 2010; Pennino et al. 2016; Poff et al. 1977; Walsh et al. 2005). Green streets programs have been implemented in some jurisdictions to capture stormwater and dry weather runoff through techniques such as bio-swales and water infiltration zones, which aim to offset the negative impacts caused by land-use changes related to urbanization (Pincetl, 2010). The cumulative effect of conventional storm water BMPs tools on the catchment scale is yet to be ascertained (Burns et al. 2012), but it has been found that the catchment wide application of distributed BMPs integrated with protected riparian buffers and forest land cover improves the hydrology compared to more centralized BMP structures (Loperfido et al. 2014).

The Piedmont region of the southeastern USA is characterized by a relatively low relief topography and malleable landscape which permits the development of dense land transportation networks; and with a relatively stable underlying geology, aids in the construction of urban infrastructure, and thus is an attractive region for urban expansion. Further, this area experiences subtropical climatic conditions with uniformly distributed annual precipitation. There is a high-density network of low order perennial intermittent streams which originate and drains this region. Fifty-eight percent of stream length in the Piedmont of NC are first order streams (NC Division of Water Quality, 2006), which provide most of the water in rivers (Boggs et al. 2013). The Catawba River sub-basin (8-digit Hydrologic Unit Code, HUC8-03050101), in which the study site is located has a Water Supply Stress Index (WaSSI) greater than one under present climatic conditions. This indicates that demand exceed the supply of water and is largely attributed to the thermoelectric power plants in the region (Averyt et al., 2013). The population projection and urban land use change for Catawba River sub-basin by 2020 is estimated to be 50%-75% and 75%-100%, respectively (Sun et al. 2008). Further, changes in land-use will have direct impacts on the surface water hydrology and associated water quality of low order streams in the region.

Mecklenburg County is located in the Piedmont region of N.C. and its current population growth rate is 12.6 percent annually, next only to Brunswick County (15 percent) and Chatham County (13.1 percent) for the state. Mecklenburg County is experiencing a 56% higher growth rate as compared to the overall North Carolina cumulative growth rate (5.5 percent). Further, the population density in Mecklenburg County is the highest (1,977 humans per square miles), among all the counties in the state (“North Carolina Budget and Management Population projections,” 2016). The increase in population has a direct relationship to the increase in urban infrastructure, which is leading to rising suburbanization trends in the outskirts of urban centers, like Charlotte and surrounding towns.

The Town of Huntersville, located in the north of Mecklenburg County, is among these growing suburban regions with the western half of the town located in the McDowell Creek sub-watershed (HUC12- 030501011401) (Figure 1). Huntersville has implemented measures to control the effect of land-use change on stormwater runoff and water quality as the McDowell Creek sub-watershed drains into a drinking water supply source for the county, Mountain Island Lake. The Huntersville Post-Construction Ordinance was adopted by the Huntersville Town Board on February 17, 2003 and incorporated into the Huntersville Zoning Ordinance. The goal of the ordinance is to establish stormwater management requirements and controls to prevent surface water quality degradation to the extent practicable in streams and lakes (Town of Huntersville, Water Quality Design Manual, 2017). The ordinance has the goal to prevent degradation of current water quality conditions and mimic pre-development runoff hydrology. The hybrid LID approach utilizes a combination of conventional Storm Water BMPs coupled with LID BMPs with the purpose of mimicking predevelopment site hydrology by storing, infiltrating, evaporating and detaining storm water runoff. As per the ordinance, impervious areas greater than 12 percent are classified as a high density development and less than 12 percent is low density. For all types of development, a minimum of 30 feet of landward buffer from all perennial and intermittent surface water is required. All types of development are required to achieve annual average 85 percent Total Suspended Sediment (TSS) removal and 50 percent Total Phosphorous (TP) removal. An annual TP load (lb/ac/year) removal requirement is also applied depending on the land use category. For Rural and Transitional Zoning Districts, the 2-year frequency, 24-hour duration storm event (3.12 inches) runoff volume is required to be treated with a hybrid LID and for all other Zoning Districts the 1-year frequency, 24-hour duration storm event (2.58 inches) runoff volume is to be treated with a hybrid LID approach. In addition, a single BMP structure cannot receive storm water runoff from area greater than five acres.

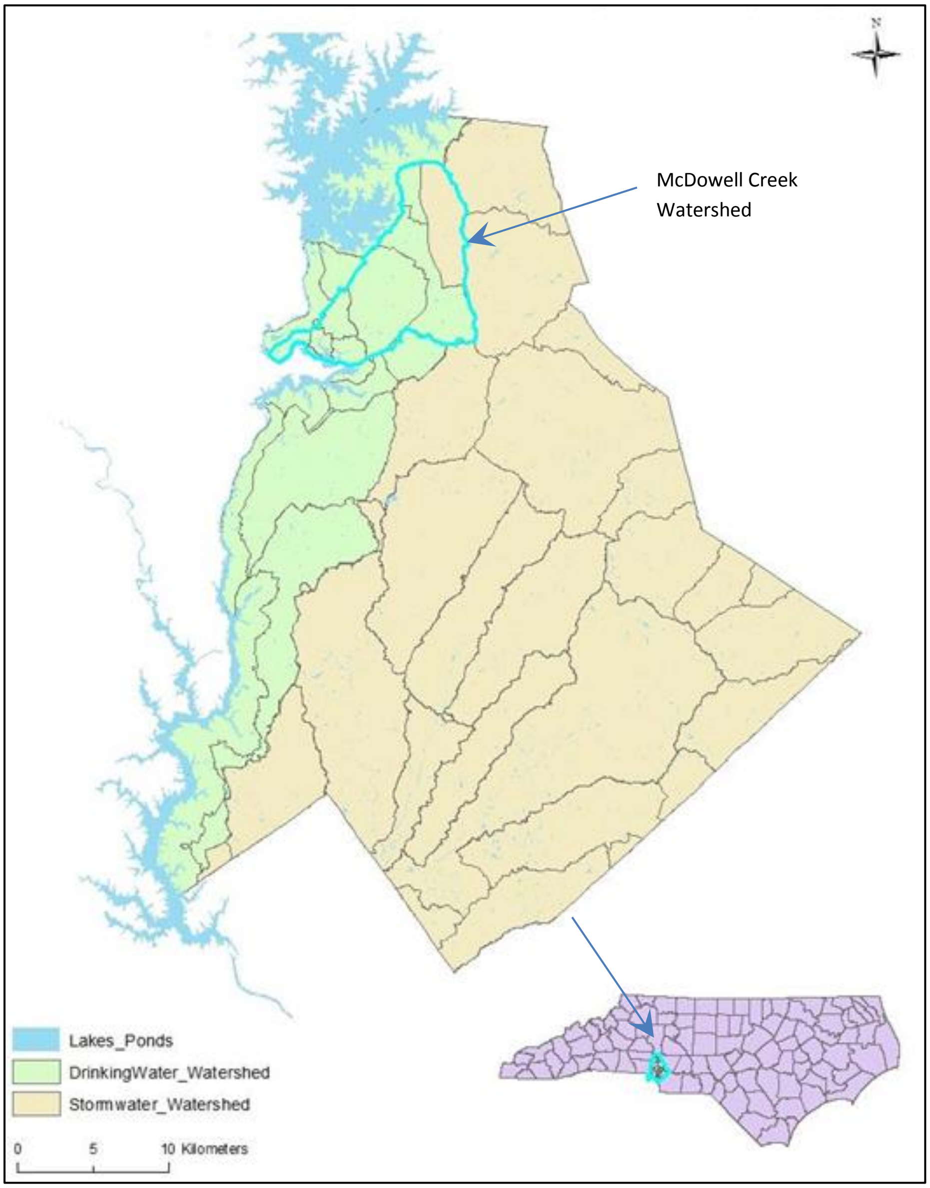


Figure 1: Location of the McDowell Creek watershed (HUC 030501011401) in Mecklenburg County

The study area for this project is located within the Town of Huntersville's metropolitan jurisdiction. The MC5 watershed is undergoing land-use conversion from agricultural and open pasture to suburban housing. The first and second order streams originating from the watershed have been restored as per the natural channel design approach (Environmental Banc & Exchange, 2013) and a riparian zone of 50 feet width on either side of the stream has been established, between the land-use conversion phases. This project seeks to ascertain the effectiveness of the measures taken to restore and maintain the hydrology and surface water quality, namely, the predevelopment channel restoration, the low impact development (LID) practices and the stormwater control measures. Towards this aim, the objective of this first phase of the project is to characterize the seasonal trends in hydrology and water quality of the study watershed.

2. LITERATURE REVIEW

2.1 The natural riverine system

A longitudinal and lateral gradient of physical, biological and chemical characteristics in natural riverine systems, as postulated by the River Continuum Concept (Vannote et al. 1980) and the Flood Pulse Concept (Junk et al. 1989), respectively, provide unifying concepts as to how natural riverine systems function. The River Continuum Concept has a longitudinal viewpoint of the system and it identifies the continuous gradient of physical conditions within a stream system, which leads to the continuous gradient of biotic mass and diversity comprising the biological system. The Flood Pulse Concept has a horizontal viewpoint of the system and it identifies the spectrum of geomorphological and hydrological conditions which produce flood pulses and it ranges from unpredictable to the predictable and short to long term duration depending on the order of stream. This pulsating mechanism incorporates the aquatic-terrestrial transition zone (riparian zone) and is crucial to the input of organic matter into the stream system. The natural hydrologic flow regime characteristics provide ecological integrity through water quality, energy sources, physical habitat and biotic interactions (Poff et al., 1977). The Upland-Riparian-Stream Continuum (Dosskey et al., 2010; Vidon et al., 2010), identifies the importance of the lateral continuum, the potential of the riparian zone in processing of nutrients and regulation of the contaminant movement to downstream waters. The effect of the subsurface, deep groundwater, hyporheic and overbank flows in combination with the overland flow (Vidon et al., 2010) creates biophysical heterogeneity in the riparian zone, which is a niche for micro-organisms in the riparian zone (Naiman et al., 2005). The disruption of these longitudinal and horizontal gradients by urbanization results in the alteration of the natural hydrologic flowpaths, morphology, and the biological and chemical composition of the riverine system (Vietz, Rutherfurd, Fletcher, & Walsh, 2016). The above concepts are important to understand the natural riverine system as well their ecological functions and these act as benchmarks for comparison with man-made structures that are developed to mimic natural ecological functions.

2.2 The Anthropocene epoch and nutrient pollution

Humans have altered the earth’s natural climate, energy and material cycles at an unprecedented rate since the 19th century. The Anthropocene epoch characterized by the advent of the industrial revolution, advances in medical science, exponential increases in world population and the use of fossil fuels that has led to human induced environmental change (Subcommission on Quaternary Stratigraphy, 2016). The increase in population has led to intensive large scale agricultural activities and livestock farming, e. g., row crop agriculture, hog and poultry battery farming as well as urbanization, all of which has significantly impacted the nitrogen, phosphorous and carbon cycles of natural systems (Carpenter et al. 1998; van Drecht et al. 2001; Galloway et al. 2004; Smith et al. 1999; Vitousek et al. 1997). In the 20th century, humans began to have an enormous impact on the global nitrogen cycle by developing industrial processes to fix atmospheric

N_2 to reactive NH_4^+ (Haber-Bosch process), new agricultural practices that boost crop yields (creation of reactive N), and the burning of fossil fuels (mobilization of reactive N). The creation of reactive N in the form of synthetic fertilizer is the largest human-induced fixation of N, followed by mobilization of reactive N by burning of fossil fuels and biomass. In 2015, the world fertilizer production was 146 Tg (Oss, 2016), whereas the estimated biological nitrogen fixation (BNF) - terrestrial rate on continents is 107 Tg per year with a continental denitrification rate of 115 Tg per year (Galloway et al. 2004). This adds up to a surplus of 138 Tg of reactive N, which is further supplemented by the mobilization of N through the burning of fossil fuels, which is estimated to be 24.5 Tg per year.

Eutrophication is caused by the addition of excess nutrients, primarily nitrogen and phosphorous compounds in water bodies. Surplus levels of nutrients act as fertilizers for aquatic plants leading to the excessive growth of algae. Increased algal mass blocks sunlight from penetrating the water, inhibiting the growth of other plants, thus a homogenous system dominated by algal blooms is created. As these algal blooms die, they are decomposed by aerobic bacteria which consume the oxygen from the water bodies, causing hypoxic conditions. The depletion of oxygen from the system leads to the death of aquatic animals and the disruption of the ecological balance in aquatic systems. This creation of dead zones in water bodies is referred to as cultural eutrophication or human induced eutrophication (Carpenter et al., 1998; Naiman et al., 2005; Smith et al., 1999; USEPA, 1998). Over time eutrophication of water bodies is a natural phenomenon and is generally characterized by a high diversity of algae (diatoms) species, but artificial or cultural eutrophication leads to a monoculture environment where only few species of algae which are nutrient tolerant remain (Mau 2000). Blue-green algae (cynobacteria) produce toxins which are detrimental to human health. Exposure can occur through drinking water as well as recreational activities. The World Health Organization (WHO) has made a provisional guideline for one of the toxins, microcystin-LR of 1 μg/L (Falconer, 1998) and the US Environmental Protection Agency

(EPA) has issued a drinking water health advisory for this toxin (“HABHRCA,” 2017). Algal toxins can accumulate in the food chain and have detrimental effects on aquatic fauna and humans (Van Dolah, 2000).

Once nutrients are introduced into the water bodies, they can be cycled internally. The aerobic bacteria (decomposers) which act on the dead algal mass, converts the organically complexed nutrients to nitrates and phosphates, which are again taken up by algae. Excessive algal growth, in response to eutrophication, can increase water treatment costs, sometimes cause treatment facilities to malfunction and are also associated with taste-and-odor problems (Dodds et al., 2009; Mau, 2000). Thus, removing the excess nutrients from aquatic systems, generally does not occur through a natural process, and requires large scale intervention, which can be capital intensive. The Total Maximum Daily Load (TMDL) approach which takes into account the point and non-point sources of pollution in the water bodies is used as a check and preventative measure to restrict nutrient pollution (Hendrickson et al. 2002; Reckhow et al., 2001). The state of North Carolina currently has no standard for total phosphorous for surface water quality. There is standard for nitrate and nitrite of 10 mg/L and 2.7 mg/L, respectively (North Carolina Surface Water Quality Standards, 2016). The US Environmental Protection Agency (EPA) recommends total phosphorous concentrations of no more than 0.05 μg/L for streams discharging into reservoirs (Oram, 2016).

2.3 Urbanization, impervious surface and runoff

Urban impervious surfaces (O’Driscoll et al., 2010) coupled with underground infrastructure such as potable water, sewer and storm-water pipes creates an altered system which bypasses natural hydrologic flowpaths. This accelerates the influx of pollutants and runoff to aquatic systems, leading to what has been labeled as the ‘urban stream syndrome’ (Meyer et al. 2005; Walsh et al. 2005). Urban runoff events are characterized by peaky short lived runoff responses, erosion of stream banks, sediment aggradation, reduced nutrient uptake and degraded biotic communities. Stream restoration strategies (Craig et al., 2008) are important ecological engineering mechanisms which if designed and implemented properly have been shown to result in the creation of more natural geomorphologic settings. This aids in the creation of diverse habitats for native biota, and increased ecological functioning such as enhanced denitrification rates (Kaushal et al. 2008). Unaltered low order head water streams with relatively low discharge typically display higher nutrient uptake rates than higher order streams (Craig et al., 2008) but are amongst the first stream channels to be replaced by storm-water drains (Kaushal & Belt, 2012).

The attenuation of polluted urban runoff is often accomplished through control measures known as best management practices (BMPs) or stormwater control measures (SCMs) (Bell et al. 2016; Gagrani et al., 2014; Jacob & Lopez, 2009; Parikh et al. 2005; Vidon et al., 2010). Nonstructural BMPs include education and on-site practices such as fertilization control or reduction, active street sweeping, good housekeeping (e.g., not disposing oils, paints and soaps in water drainage systems), and zoning restrictions to limit population densities (Jacob & Lopez, 2009). Structural BMPs, are physical structures that collect and treat runoff. Treatment usually consists of filtration, detention, retention, and/or infiltration. The most commonly used BMPs include storm water wetlands and ponds, of appropriate type, location and sizing to optimally replenish groundwater recharge and reduce peak stormflow discharge. Other BMPs include grassed swales, pervious pavements, green roofs, infiltration trenches, and sand filters (Jacob & Lopez, 2009). It is generally recommended that land-based BMPs should be employed before in-channel stream restoration approaches, and includes repairing sewer infrastructure, minimizing nitrogen and phosphorous applications and the construction of retention ponds and other bioretention structures (Craig et al., 2008). Retention structures can aid in both contaminant reductions through sedimentation, the adsorption of contaminants onto sediment particles, filtration, denitrification, immobilization through uptake by both plants and microorganisms and limiting the overland runoff into streams. In high density impervious settings, the stormwater retention ponds can reduce flow and improve water quality, if positioned and sized properly (Gagrani et al., 2014; Jacob & Lopez, 2009). A watershed scale approach should be used to plan these structures, rather than simply addressing reach scale targets. The watershed scale approach in planning the installation of these structures will take into account the overall natural drainage pattern of the region and the other land use changes happening in the area, thus, increases the overall functionality of the stormwater controls. At present storm-water management structures are designed and planned for site specific scales and phase-by-phase design to meet the mandatory water quality and storm water targets. This piecemeal, meet-the-target approach is often not successful in attaining the objective of improving overall water quality in developing watersheds (Gagrani et al., 2014).

2.4 Surface hydrology study unit

The catchment or watershed as determined by the topographic divide, is the hydrologic unit chosen to examine surface hydrological processes as it represents a definable system where the fluxes of energy and water can be quantified (Black, 2005). Depending on the scale of study (both in space and time dimensions), various methods have been developed to study the streamflow runoff, its sources, dynamics, pathways and chemical composition (Peters, 1994). This information is crucial to understanding the characteristics of catchments and the development management measures to mitigate extreme hydrologic events. These include droughts and floods, but also include a range of storm types from long-duration, low-intensity storms to short-duration, high-intensity storms. Extreme events are also increasingly related to major human related alterations of the landscape through conversion from one land-use to another, such as deforestation and the urbanization of agricultural areas. Additional factors that can dramatically alter watershed hydrology include fire, landslides and volcanism. All of these factors can have a pronounced effect on the physical, chemical and biological characteristics of a catchment and, in turn, these can affect the hydrology of the system (Peters, 1994).

Evapotranspiration, infiltration and storage are three controlling factors which are responsible for the characteristic discharge hydrology of a region and these are often altered during the process of urbanization. Evapotranspiration in forested areas in the southeastern United States ranges from 50 to 90% of precipitation inputs (Boggs and Sun 2011). A long term (2000-2007) analysis of the hydrology of forested and urban watersheds in the Piedmont region showed that differences in these three factors occurred more during the growing season as compared to the dormant season. The mean annual discharge coefficient and peakflow rate were significantly higher in urban watershed compared to the forest watershed. That study concluded that this difference was partially due to reduction in evapotranspiration in the urban watershed.

The Beaverdam Creek Watershed long term study (2003-2012) in the North Carolina Piedmont (Allan et al., 2013) showed that phase-by-phase implementation of stormwater control measures (SCMs) in a suburbanizing watershed (BD4) did not achieve the mandatory reduction of peak flow storm water volumes, and the implemented SCM network reduced the runoff volume by 3%. The study recommended the importance of watershed scales stormwater management plans with incorporation of natural wetland and floodplain areas (Gagrani et al., 2014). The study used multiple approaches to understand the runoff hydrology of the urbanizing watershed, namely, unit hydrograph, unit impulse and Mann-Kendall trend test and all approaches gave similar results. The stromwater detention basins in most developed watersheds (BD4 and BD3) lead to declines in peakflow discharge but increase in runoff duration and runoff coefficient; whereas a stream restoration without the implementation of SCM on the BD2 watershed had the least impact on runoff response (Gagrani, 2013).

Urban expansion is leading to the formation of engineered hydrologic flowpaths coupled with natural hydrologic flowpaths (Kaushal & Belt, 2012). Lower order streams are replaced by urban infrastructure because it is easier to construct in these areas and form artificial flowpaths.

The joints and cracks in utility conduits and tunnels contribute significantly to groundwater and baseflow in urban streams (Sharp et al. 2006). The urban watershed continuum (Kaushal & Belt, 2012) provides a framework for analyzing the urban watershed in four identified dimensions (viz., longitudinal, lateral, vertical and temporal). That study identifies trends in urban systems as: the replacement of low order head water streams by urban infrastructure (longitudinal dimension); the removal of riparian zones because of urban proliferation (lateral dimension); the establishment of an underground network of storm-water, sewer and water pipes (vertical dimension); and the aging of the urban infrastructure (temporal dimension). Understanding and assessing the impacts caused by urbanization in these four dimensions can aid in formulating corrective measures and structures to offset urbanization's negative impacts. The LID technologies designed to mimic the natural hydrologic flowpaths are designed to recharge groundwater by infiltration and harvesting urban runoff as potential solutions for restoring natural water balance (Askarizadeh et al., 2015).

2.5 Hydrological transport

The chemical composition of stream water is modified by temporally changing hydrological processes, including the position of the water table, variable flowpaths and variable contributions of geologically controlled groundwater composition (Rice & Bricker, 1995). A long-term study (1982 – 1993) on two forested watersheds in the north-central Maryland (underlain by the Precambrian Catoctin Formation), illustrated the difference between the chemical composition of stream water during the growing (summer and autumn - dry) season and the dormant (winter and early spring - wet) season (Rice & Bricker, 1995). During the growing season, the water table was below the regolith - bedrock interface, and as a result of prolonged contact with relatively unweathered bedrock, stream water becomes rich in cations, alkalinity and dissolved silica. Precipitation during the growing season generally does not reach the ground water reservoir, thus stream-composition reflects bedrock derived components. During the dormant season the evapotranspiration is low and hence most of the groundwater recharge happens during this time and the water table rises into the regolith above the bedrock. The presence of sulfates contributed from wet and dry deposition makes the stream water acidic, low in alkalinity. Further, during the dormant season, shallower hydrologic flowpaths in the regolith and lesser residence time of groundwater as compared to the growing season, leads to lower concentrations of dissolved silica. Nitrate concentrations in streams draining a suburban watershed ranged between those found in forested and agricultural watersheds, which represent the lower and upper extremes measured in the Baltimore LTER study (Kaushal et al. 2008). In addition, a seasonal pattern, in nitrate concentrations was identified in stream water for all three different land use watersheds. The nitrate concentration was highest during the wet season and lowest during the dry season. It was also found that annual nitrate concentrations were highest in extreme wet years and lowest during low flow periods, and moderate for those years with average annual precipitation (Kaushal et al. 2008).

Suspended sediment in the stream water is one of the major components of non-point source pollution caused by overland flow and channel erosion. A number of particulate bound pollutants, including phosphates, metals, oil and grease, and pesticides are found in stormwater runoff. Strong relationships between the concentrations of total suspended solids and copper, lead, and zinc during storm events has been observed in urban watersheds in Baltimore City (Bain et al. 2012; Kaushal and Belt 2012). The pollutants associated with suspended sediments can enter the food chain through small aquatic life, eventually entering the tissues of fish and humans (U.S. Environmental Protection Agency (EPA), 2005). The turbidity of the water is often linked to the suspended sediment concentrations. High turbidity levels limit the sunlight entering the water column, which can impact primary productivity and reduce the abundance and diversity of aquatic biota. It is universally observed in watersheds with a variety of land uses, that the first rain event after a prolonged dry period, often contributes higher sediment loads than subsequent storms.

As the MC5 watershed is undergoing land use change during the study period, converting from pasture and forest landcover to suburban residential, there is ongoing active construction occurring during the study period. The analysis of the water quality with respect to total suspended sediments (TSS) and turbidity is expected to show increasing sediment loads until land cover stabilization. It is expected that, during the active construction phase, high intensity rainfall after prolonged dry periods will show a sudden peak in TSS and turbidity levels in the stream water. Though this is a natural phenomenon of the overland runoff delivery of TSS, turbidity and other pollutants, the TSS load is generally increased during the active construction phase (Allan et al., 2013; Carpenter et al., 1998; Gagrani et al., 2014). This increase is related to site preparation and construction activities, which exposes extensive areas of bare soil for prolonged periods. Further, the underground network of stormwater, potable water and sewer pipes is laid after the land clearing and before the above ground construction, which further intensifies the soil disturbance. The top soil is scraped off from the surface, and extensive cut and fill activities and excavation to install subsurface infrastructure further disturb the soil profile. Thus, the present practice of active construction is a leading cause of extreme TSS loads from construction sites. A study on sources of suspended sediments in southern Piedmont streams had found that 23 to 30 percent of suspended sediment originate from upland subsoil sources like construction sites and unpaved roads (Mukundan et al. 2010). Erosion control measures, like silt fencing and gravel bars often fail during high intensity rain events (as per the observation of construction activities at the MC5 site during May 2016). Further, the particles responsible for high turbidity is mainly clay and silt sized particles and constitute 92 % of TSS. The openings in the fabric of geotextile is approximately 600 μm, whereas the particle diameter of silt and clay is 60 μm, which leads to ineffectiveness of geotextile silt fences to reduce turbidity (Barrett et al. 1998). In a study of effectiveness of sediment control measures, namely, compost application, hydroseeding and silt fencing, it was found that compost application containing organic nutrients significantly reduced runoff volume and erosion potential, relative to hydroseeding and silt fencing (Faucette et al., 2005).

3. RESEARCH QUESTION AND HYPOTHESES

The overall research objective of the long-term MC5 study (2015-2025) is to identify the impact of low impact development (LID) practices and storm-water control measures (SCMs) on the hydrology and hydrochemical transport of a suburbanizing Piedmont watershed. This current project (June 2015 – December 2016) was a first phase of this long-term study. The research question which this project addressed was “what were the seasonal characteristics of the hydrology and hydrochemical transport, during the project period (June 2015 – December 2016)?” The question that guided this research: Was there a difference in the hydrology and hydrochemical transport between the growing and the dormant seasons of the MC5 watershed during this time period?

To address this question, the hydrology and hydrochemical transport characteristics of the growing and dormant seasons were compared. The growing season was defined as the time period from April to September, and the dormant season was the time period from October to March.

This study computed the monthly hydrology of water year 2016 and 2017 (October 1, 2015 to September 30, 2017), and the data analyzed to determine seasonal characteristics. The concentrations for the 27 water quality constituents from May 26, 2015 to December 31, 2016 were analyzed for significant differences between the dormant season base flow, dormant season high flow, growing season base flow and growing season high flow. The growing and dormant seasons hydrochemical transport of water year 2016 (October 1, 2015 to September 30, 2016) was computed and analyzed. The mass balance of the growing season of water year 2016 (April 1, 2016 to September 30, 2016) was computed and analyzed.

The null and alternative hypotheses for the two aspects of research, namely, hydrology and hydrochemical transport were:

3.1 Hydrology

Null Hypothesis (H_0)

There is no significant difference in the hydrology of the study area between the growing and dormant seasons.

Alternative Hypothesis (H_1)

There is significant difference in the hydrology of the study area between the growing and dormant seasons.

The precipitation is relatively uniformly distributed throughout the year in this region of the NC Piedmont, with no significant difference between the dormant and growing season precipitation (Table 1). The normal total dormant season precipitation is 52.15 cm and the normal total growing season precipitation is 53.59 cm. The average air temperature is significantly different between the two seasons, with normal mean dormant season temperature 59 percent less than the normal mean growing season temperature. The mean normal temperature for the dormant season is 8.95 ^{o}C and the mean normal temperature for the growing season is 21.92 ^{o}C. The growing season temperature is adequate for plant growth, which leads to higher evapotranspiration during the growing season. Further the plant activity during the growing seasons consumes the soil moisture and shallow groundwaters. Thus, the stream discharge, runoff, soil moisture and groundwater levels are expected to be significantly higher during the dormant season as compared to the growing season. Conversely, the evapotranspiration will be significantly higher during the growing season as compared to the dormant season. These seasonal characteristic trends of hydrologic parameters between the two seasons, would be expected to support the alternative hypothesis.

3.2 Hydrochemical transport

Null Hypothesis (H_0)

There is no significant difference in the unit area hydrochemical transport from the study area between the growing and dormant seasons.

Alternative Hypothesis (H_1)

There is significant difference in the unit area hydrochemical transport from the study area between the growing and dormant seasons.

It is expected that the chemical composition of water, namely total carbon, nitrogen, phosphorous and the major ion concentrations, should show distinct seasonal trends because of the difference in the biotic activity between the two seasons. With similar input of precipitation during both the seasons, but with significant air temperature difference, the hydrologic flowpaths are expected to be affected, with dormant season characterized with shallower flowpaths and the growing season with deeper hydrologic flowpaths, which in turn will effect the stream water chemistry.

The dormant season which is characterized by lower air temperatures and lower biotic activity, is expected to have higher stream water concentrations of carbon, nitrogen and phosphorous compounds, but lower major ionic concentrations because of dilution of stream water by precipitation. Further, the water table is relatively higher during the dormant season, and thus groundwater has lower residence time, leading to lower ionic composition of stream water. Conversely, the growing season is characterized by warmer temperatures, leading to higher biological activity in the stream and the riparian area, which in turn consume nutrients. Thus, the biologically active carbon, nitrogen and phosphorous compounds in stream water are expected to be lower during the growing season as compared to dormant season. At the same time, the ionic composition of water during the growing season will be relatively higher because of lower dilution by precipitation. Also, with the groundwater table being lower during the growing season, will result in a longer residence time, and the input of this groundwater will increase the ionic composition of stream water. Thus, the ground water in the baseflow during the growing season is expected to have a higher ionic composition as compared to baseflow during the dormant seasons.

4. METHODS

4.1 Study design and statistical analysis

4.1.1 Hydrology

The hydrology of the study sites was analyzed using the water balance approach. The water balance continuity equation is:

$$P = Et + Q \pm \Delta S \quad (1)$$

where P = precipitation, Et = evapotranspiration, Q = stream discharge, and ΔS = change in storage (principally, groundwater and soil moisture levels)

For this study precipitation, soil moisture and groundwater levels were measured on site. A tipping bucket recording rain gauge and standard rain gauge were used to measure the precipitation amount and its intensity. Potential evapotranspiration was estimated by the Thornthwaite Equation (Thornthwaite, 1948) using climate data measured at the Charlotte Douglass Airport station. Six Campbell Scientific soil reflectometry probes measured soil moisture at six different locations along two transects from the stream channel to the edge of the riparian zone. Groundwater levels were monitored with shallow groundwater wells, which were installed at eleven different locations in the conservation easement areas, as part of the five-year post-wetland restoration monitoring program. Water levels and discharge were recorded continuously at the watershed outlet, by the United States Geological Survey (USGS).

The different hydrology components, namely precipitation, evapotranspiration, discharge, soil moisture and groundwater levels were compared for the growing and dormant season, to understand characteristic trends of these hydrologic components during the study period. The hydrologic analysis of the study period will be a benchmark for the continuing comparative study, as the landuse change of the watershed progresses.

4.1.2 Surface water quality and hydrochemical transport

The surface water of the study area is classified as Water supply IV (WS-IV) and suitable for Class C uses as per the classification developed by North Carolina Department of Environmental Quality (North Carolina Surface Water Quality Standards, 2016). The WS-IV classification means that the surface water is a drinking water source, is also used for secondary recreational purpose which involves human contact, and is drained from moderately to highly constructed watersheds. As per this classification, the surface water quality standards developed by NC DEQ and US EPA (15A NCAC 02B Surface Water Standards 2016) apply to the surface water quality of water draining from the study watershed.

The NC surface water quality standards were used as the reference for comparison to assess the water quality of the study watershed. The parameters which were measured / analyzed were: pH, specific conductance (SC), turbidity, total suspended solids (TSS), total organic carbon (TOC), dissolved organic carbon (DOC), total nitrogen (TN), total dissolved nitrogen (TDN), nitrate (NO_3^- as N), ammonium (NH_4^+ as NH_4^+), total phosphorous (TP), total dissolved phosphorous (TDP), ortho-P (PO_4^{3-} as P), major cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) and major anions (F^-, Br^-, Cl^-, SO_4^{2-}). Particulate organic carbon (POC) concentration was calculated as a difference between TOC and DOC concentrations. Particulate nitrogen (PN) was calculated as the difference between TN and TDN concentrations. Dissolved organic nitrogen (DON) concentration was estimated by subtracting nitrate and ammonium concentrations from TDN concentration. Particulate phosphorous (PP) concentration was calculated as the difference between TP and TDP concentrations. Dissolved organic phosphorous (DOP) was calculated as the difference between TDP and ortho-P concentrations. To estimate the amount of bicarbonates (HCO_3^-), the total charge equivalence of anions is subtracted from the total charge equivalence of cations. Thus, total 27 water quality constituents were analyzed / estimated from each grab sample. The laboratory procedure of analysis and calculation of the above water quality constituents are discussed in the following laboratory methods section.

Three major frameworks were deployed for the analysis of the surface water quality and hydrochemical transport. All the approaches were based on the measurement of parameters from grab water samples. The underlying assumption was that the concentration of the hydrochemical constituents and other water quality parameters measured by each grab sample was a representative of the average concentrations for the volume of water between two consecutive sampling time periods. The field sampling procedure and laboratory analysis are discussed in the following field and laboratory methods section.

4.1.2.1 Water quality concentrations

The concentrations for each of the hydrochemical components was derived from the individual water samples. The samples were subdivided as per the season (dormant season and growing season) and flow type (base flow and high flow), which lead to four groups, namely, dormant season base flow (DSBF), dormant season high flow (DSHF), growing season base flow (GSBF) and growing season high flow (GSHF). When the sample was collected during no rain period, it was labelled base flow, and when it was collected during a rain event, it was labelled high flow. There were a total 301 grab samples collected during May 26, 2015 to December 31, 2016, and these were divided into four groups (Table 1).

Table 1: Grab samples collected from the outlet of the MC5 watershed are divided into four groups, namely, dormant season base flow (DSBF), dormant season high flow (DSHF), growing season base flow (GSBF) and growing season high flow (GSHF), (from May 26, 2015 to December 31, 2016)

Groups	Grab water samples (n)
DSBF	93
DSHF	64
GSBF	106
GSHF	38
Total	**301**

The concentrations of water quality constituents between the four groups was compared statistically. The time of the year, categorized for the season was the independent variable, the measured concentration of the water quality constituents was the dependent variable. Data from all 301 grab samples for all the 27 water quality constituents were tested for normality by performing the Shapiro Wilk Normality test. A significance value (p value) of 0.05 or less was used to accept the alternative hypothesis. If the components showed significant deviation from the normal distribution, a log transformation was applied to the data and again tested for normality. If after the log transformation of the data, the sample distribution still deviated from a normal distribution ($p < 0.05$), then the non-parametric equivalent analysis of variance, that is the Kruskal Wallis H test was used to ascertain the difference between the four groups, namely DSBF, DSHF, GSBF, GSHF. In all the cases after the application of Kruskal Wallis H test where the significance value was less than 0.05, a post-hoc test was applied, to identify the specifically which groups differed from one another. In the case of a normal distribution of data for any of the 27 water quality constituents, a parametric test, namely the one-way analysis of variance was used to determine the differences between the four groups. Since the samples size of each of the four groups was different, a repeated measures analysis of variance could not be used for this analysis.

4.1.2.2 Hydrochemical transport

This analysis was designed to determine the amount of transport of different water quality constituents during different seasons, namely the growing and dormant seasons. Parameters measured by water quality probes (namely, turbidity and conductivity) a volume weighted approach was used to determine seasonal volumetric averages. The rest of the water quality constituents, which were measured as concentrations (example: milligram per liter), the concentration was multiplied with the representative volume of discharge and the totals then divided by area of the watershed and depth of precipitation for the period, to determine the yield per unit area per unit depth precipitation. The hydrogen ion microequivalent per liter was computed from the pH measurements, using the formula:

$$H^+ \ \mu eq/L = 10^{(-pH)} * 10^6 \quad (2)$$

4.1.2.3 Mass balance

This analysis was designed to determine the retention or export of specific water quality constituents from the watershed during the seasons (Equation 4).

$$\text{Input} - \text{Output} = \text{Net retention or export} \quad (4)$$

The water quality constituents in the bulk precipitation were the input components and the water quality constituents in the stream water samples collected from the watershed outlet points were the output components. The difference in the hydrochemical transport of the output water quality constituents from the input water quality constituents gave the net retention or export of those constituents from the watershed for that particular time period. This information was used to help understand the biogeochemical processes in the watershed for the specific season (Bormann & Likens, 1967; Likens, Bormann, Johnson, & Pierce, 1967).

4.1.3 Error analysis

To determine the confidence intervals for the for the dormant and growing seasons, two types of uncertainties were estimated, the estimated discharge uncertainty and the estimated laboratory chemical analysis uncertainty. The discharge uncertainty was estimated to be 12 %, derived from the literature (Harmel, Cooper, Slade, Haney, & Arnold, 2006; Winter, 1981). To estimate the laboratory chemical analysis uncertainty, the average standard deviation for each of the parameters was determined by averaging the individual standard deviation of randomly measured quintuplicate samples during different runs of the samples. The coefficient of variation was computed from the average standard deviation for each chemical constituent to determine the confidence limit for each of the parameters measured. An analytical uncertainty of 2 % to 18 % was determined by quintuplicate replication of the water quality constituents. The of the water quality constituent was a cross product of the hydrology parameters and the concentrations determined by chemical analysis. Thus, one standard deviation of the measured value was used to estimate the cumulative error (Allan, Roulet, & Hill, 1993; Barry & Morris, 1991; Harmel et al., 2006).

4.2 Field methods

Stream water samples were collected at least three times a week from the outlet point and once a week from the three tributaries, viz., Tributary North, Tributary West and Tributary East (Figure 2). In this study, only the analytical measurements of stream water outlet sample are incorporated for water quality constituents concentration, hydrochemical and mass-balance analysis. Rainfall forecasts are monitored closely and water samples were collected before, during, and post rain events. Samples were collected whenever rainfall was expected to exceed 0.64 cm (0.25 inch). Multiple water samples were collected during rainfall events of more than 1.27 cm (0.50 inch). A monitoring station was installed by UNC Charlotte researchers in the conservation easement area between the outlet point and the junction of the three tributaries. The station contains a Campbell Scientific CR10x datalogger, a manual rain gauge, a tipping bucket rain gauge, a bulk precipitation collector, and monitors six Campbell Scientific soil moisture probes. Rainfall and soil moisture were measured on a 15-minute time step. Manual readings are collected weekly and the bulk precipitation was analyzed for the same suite of parameters as stream water. During the dormant season (October to March) when snow was expected, the funnel from the standard rain gage was removed and then during weekly collection, it was melted and measured in the calibrated tube of the rain gauge. The stage height at the outlet point was noted during sample collection from the USGS stream gage installed at the watershed outlet. The USGS gaging station 0214265828 at McDowell Creek Tributary at SR 2131 near Hicks Crossroads, NC provides the gage height and discharge at the site on a 5-minute time step. The groundwater levels from eleven groundwater wells monitored by the consulting firm, Kimley Horn, was used in the water balance calculations help estimate storage change between the growing and dormant season.

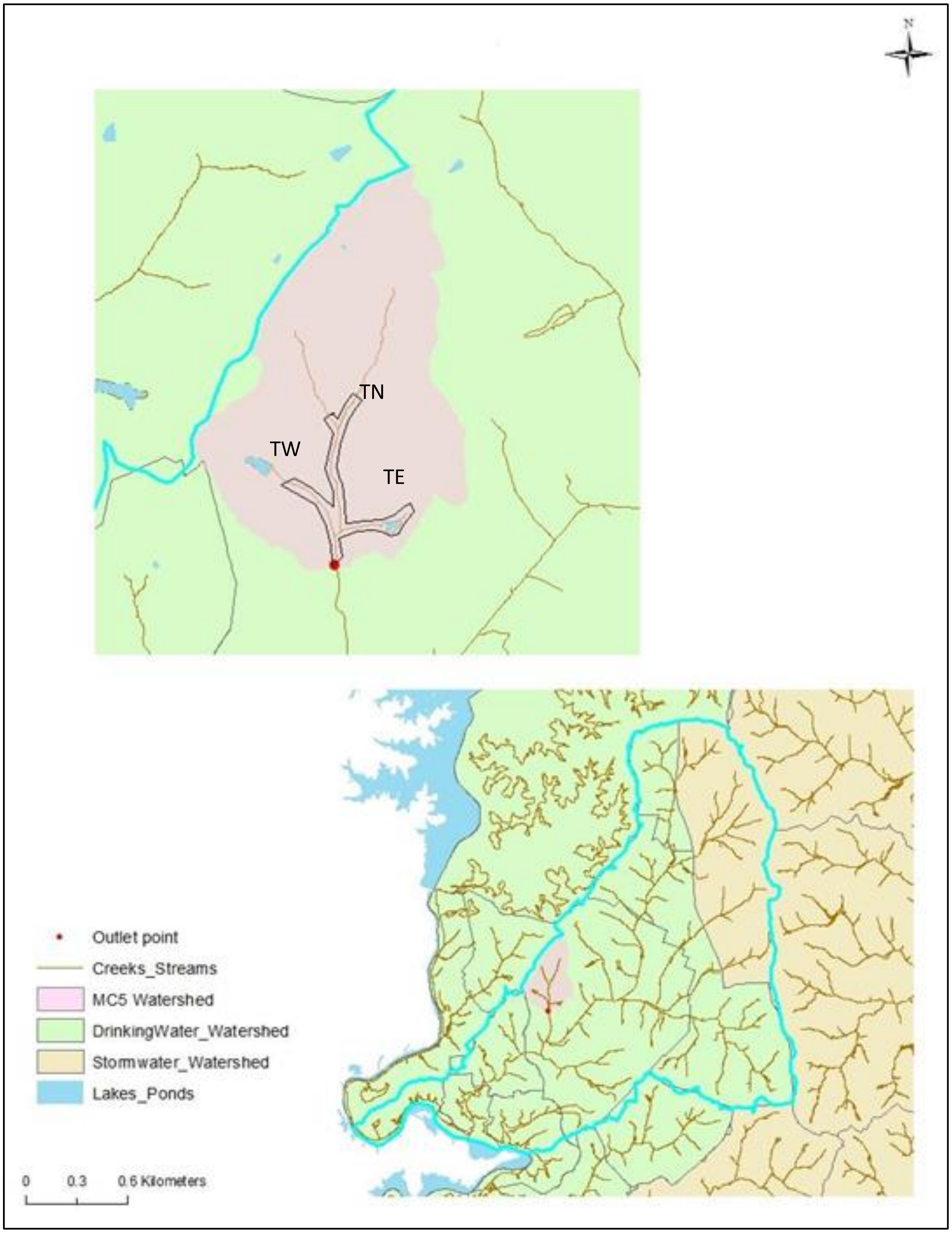


Figure 2: Location of the study watershed, Mecklenburg Catawba 5 (MC5) in the McDowell Creek watershed. Tributary East (TE), Tributary West (TW), and Tributary North (TN)

4.3 Laboratory methods

4.3.1 Preliminary processing of water samples

Water samples collected from the field site were brought to the Hydrology and Biogeochemistry laboratory at the University of North Carolina at Charlotte and generally processed within 24 hours of collection. Firstly, they underwent preliminary processing, which included the measurement of pH, specific conductance, turbidity, and total suspended sediments (TSS) on unfiltered water samples.

The pH of the water sample was measured using an Oakton pH meter standardized to buffers of pH 4 and 7. The specific conductance was measured with the Hanna Instruments 9033 temperature compensated multi-range conductivity meter. The meter was standardized to a 140 µS standard solution. Turbidity was measured with a Lamotte 2020 turbidimeter, calibrated with standards of 1 NTU and 10 NTU before each measurement. TSS was determined by vacuum filtering a known volume of water sample through 0.45 µm filter paper. The filter paper with the suspended sediments was dried in an oven with constant temperature of 105 ^{o}C. The difference between the dried filter paper with sediments and the initial weight of the filter paper, provided the sediment weight for the volume of water sample filtered, which was then converted into the unit milligrams per liter of TSS (APHA, 1992).

4.3.2 Preservation of filtrate and unfiltered water samples

The water sample was suction filtered using 0.45 µm filter paper. One hundred twenty milliliters of filtrate were stored for the later processing of Dissolved Organic Carbon (DOC), Total Dissolved Nitrogen (TDN), Dissolved Total Phosphorous (DTP), and major anions. A second subsample, 60 ml of filtrate was preserved by adding one drop of 8M HCl for later analysis of major cations. A third 120ml unfiltered subsample was stored for processing of Total Organic Carbon (TOC), Total Nitrogen (TN) and Total Phosphorous (TP). The three subsample bottles were stored in a freezer until further chemical analysis.

4.3.3 Secondary processing of preserved water samples for chemical composition

A Shimadzu TOC-V analyzer with a TN module was used to measure Total Organic Carbon (TOC) and Total Nitrogen (TN) from the preserved unfiltered samples. The same analyzer was used to measure Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN) from the preserved filtered subsamples. The analyzer works on the principle of combustion and catalytic oxidation of carbon and nitrogen present in the water samples to carbon dioxide and nitrogen mono oxide at 680˚C and 720˚C respectively and detection of these gases by a Non-Dispersive Infrared Detector (NDIR) and Chemiluminescence detector, respectively (*Shimadzu TOC-V Series*, 2001).

The ionic composition of water samples was measured using the Dionex DX-500 Ion Exchange Chromatograph system. The major cations measured were Na^+, Ca^{2+}, NH_4^+, Mg^{2+}, K^+ (IonPac®CS12 column) using the filtered sample preserved with HCl. The major anions measured were F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-} (IonPac®AS22 column) using the thawed filtered subsample. The working principle of this method is separation of the ions in an eluent (buffering solution), based on differential migration as it passes over an oppositely charged analytical column (Dionex Corporation, 2002).

The Total Phosphorous (TP) in the unfiltered sample was determined manually by the ascorbic acid method following a digestion step (HACH Company, 2013). The Total Dissolved Phosphorous (TDP) was determined with a Lachat QuickChem 8500 auto analyzer ("QuikChem ® Method 10-115-01-3-A Determination of Phosphorous by FIA Colorimetry (in-line persulfate digestion method)," 2009), using the same ascorbic acid method with Flow Injection Analysis (FIA) and Photometric detection.

5. STUDY AREA

5.1 Location and area

The MC5 watershed is located at approximately 35 ° 24 ' 06.52 " latitude and 80 ° 55 ' 03.79 " longitude, in the McDowell Creek watershed (12 digit HUC 030501011401). The McDowell Creek watershed is in the Catawba River basin (Upper Catawba, 8-digit HUC 03050101). The watershed is located in the Town of Huntersville in northern Mecklenburg County, North Carolina (Figure 1 and 2). The area of the study watershed is 2.33 km^2 (Environmental Banc & Exchange, 2012). The land was historically used for row crop farming and then as open pasture field for livestock rearing. At present a residential subdivision is being constructed on the watershed.

5.2 Geology and soils

Topographic relief at the site ranges from 201 to 238 meters above mean sea level. The land slopes generally from the North to the South. Bedrock in this region consists of a mixture of felsic crystalline and mafic rocks. Soils in this region are typically high in clay. No major geologic features (faults, fractures, etc.) are present on or near the site; therefore, it is reasonable to assume that, the direction of near-surface groundwater flow under static conditions for most of the site approximates the surface topography of the site (Environmental Banc & Exchange, 2012). Mapped soils on the site include Cecil, Enon, Mecklenburg, Monacan and a small area of Pacolet. All of the land area where the 2012 stream restoration activities took place is comprised of the Monacan soil unit. These soils are characterized as having a fine-loamy texture, mixed thermic, are poorly drained and, moderately permeable formed from recent alluvium. The organic content is low in the surface layer, permeability is slow and runoff is medium (Environmental Banc & Exchange, 2012). A Hydric soil investigation was performed by a licensed soil scientist and professional wetland scientist on September 30, 2011 at the site. A visual survey was conducted and 66 hand-turned soil auger borings were made. The wetland areas within the watershed were delineated from this investigation and were found to contain buried hydric soils (Environmental Banc & Exchange, 2012).

5.3 Air temperature and precipitation

The MC5 watershed lies in the humid subtropical climate zone (Cfa) in the Köppen climatic 14 classification. The 30-year normal (1971-2000) monthly mean, minimum, and maximum temperatures are 15.5 ° C, 4.5 °C (January), and 25.8 °C (July), respectively, and the mean annual precipitation is 106 cm ("National Oceanic and Atmospheric Administration," 2016). November 2015 was the wettest November as compared to the November's from year 1878 to 2017, with the record 25.50 cm of precipitation. December 2015 (13.0 ºC) and February 2017 (11.9 ºC) were the warmest December and February months from year 1878 to 2017. Figure 3 and Table 2 depicts the precipitation and air temperatures for year 2015 to 2017 and latest 30 year normals.

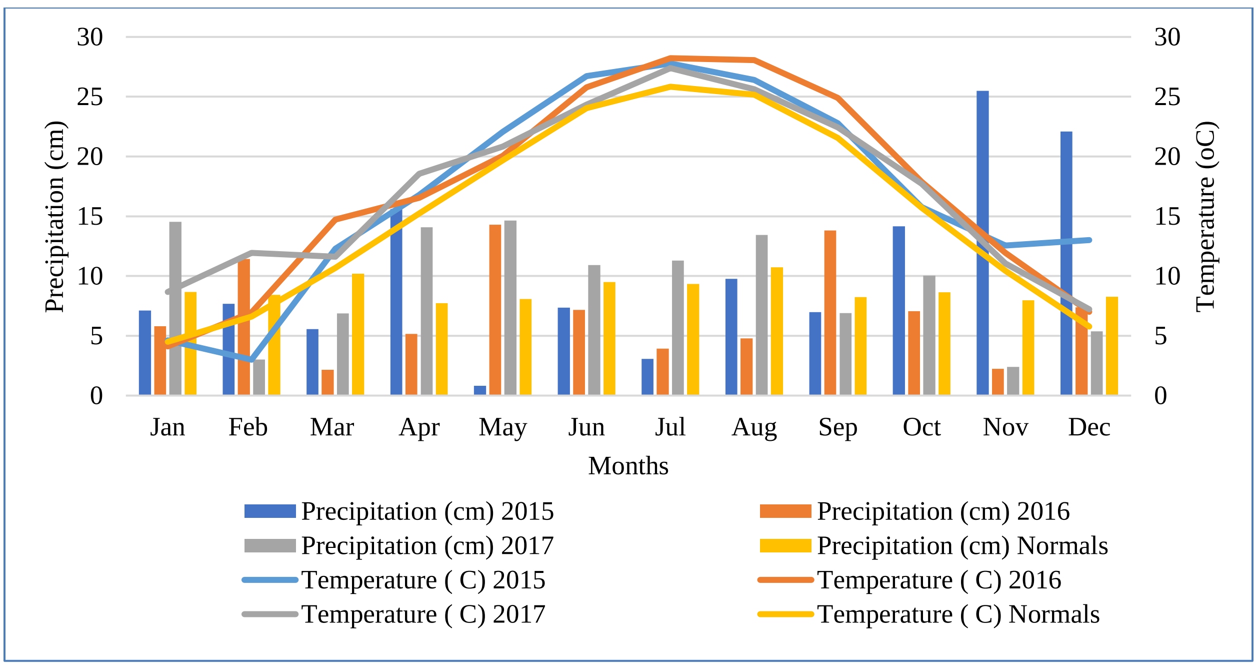


Figure 3: Climograph of Charlotte, NC for year 2015, 2016 and 2017 and normals of temperature and precipitation (Source: Data from National Weather Services, NOAA, http://www.weather.gov/gsp/cltcli)

Table 2: Precipitation and air temperature data for year 2015, 2016 and 2017 and climate normals for Charlotte (Source: Data from National Weather Services, NOAA, http://www.weather.gov/gsp/cltcli)

	Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Precipitation (cm)	2015	7.11	7.67	5.56	15.60	0.81	7.37	3.07	9.75	6.99	14.15	25.50	22.10
	2016	5.79	11.43	2.16	5.16	14.30	7.16	3.94	4.78	13.82	7.06	2.24	7.39
	2017	14.53	3.02	6.88	14.07	14.63	10.92	11.30	13.44	6.91	10.03	2.39	5.38
	Normals	8.66	8.43	10.19	7.72	8.08	9.50	9.35	10.72	8.23	8.64	7.98	8.26
Temperature (ºC)	2015	4.6	3.0	12.3	16.8	22.1	26.7	27.8	26.4	22.8	15.8	12.6	13.0
	2016	4.1	6.9	14.7	16.6	20.1	25.8	28.2	28.1	24.9	17.9	11.9	7.0
	2017	8.7	11.9	11.6	18.6	20.8	24.3	27.4	25.6	22.4	17.7	11.1	7.2
	Normals	4.5	6.6	10.7	15.2	19.7	24.1	25.8	25.2	21.6	15.7	10.4	5.8

5.4 Ecological condition

The first and second order streams arising from this watershed are natural perennial / intermittent streams and are tributaries to Lower McDowell Creek which drains into the Mountain Island Lake, which is a drinking water supply source for the County (Figure 1, 2). McDowell Creek is classified by the NC Department of Environmental Quality (NCDEQ) as a Water Supply Stream (WS-IV, Protected Area). Lower McDowell Creek was on the 303(d)-listed stream. For the years 2000 to 2010 and was categorized as having ‘Overall impaired Biological Integrity’ (NC 2010 Integrated Report Categories 4 and 5 Impaired Waters, Category 5-303(d) List Approved by EPA August 31, 2010). It is on the 305(b) list for year 2014 for ‘Impaired benthos biological integrity and Mercury in fish tissue (305(b) Assessed Waterbody History Report for NC11-115-(1.5) b) (City of Charlotte NPDES MS4 Permit Program Stormwater Management Program Plan 2015, City of Charlotte Mecklenburg County NPDES MS4 Permit Program TMDL Watershed Plan 2015).

In 2002, the North Carolina Wetlands Restoration Program identified McDowell Creek as a ‘Targeted Local Watershed’, noting a downward trend in water quality. Turbidity from excess sediment was the major impairment identified in McDowell Creek. Also, this watershed was and continues to be rapidly urbanizing and the loss of forest and increases in the impervious surface cover having led to increased storm water runoff causing impairment of the overall biological integrity of the stream. The McDowell Creek Watershed Management Plan was developed in 2006 by Mecklenburg County, and provides a comprehensive roadmap for the management and restoration of surface waters in the entire watershed.

5.5 Historic land use and stream restoration

Historically, the MC5 watershed was used for agricultural and in particular livestock production with a few rural single-family residences and open pasture with some areas of managed forest. Agricultural activities contributed to significant modifications of the surface water flowpaths, the water balance and vegetation communities. The stream channels were degraded with incised straightened channels, eroding banks, wetland ditching, and impoundment. The first and second order streams originating from this watershed (approximate total original stream length of 2370 m) were restored in the year 2012 by implementing the Natural Channel Design and Bioengineering approaches (Environmental Banc & Exchange, 2013), resulting in 2,930 m of stream restoration, 305 m of stream enhancement, including the establishment of a 0.107 km^2 riparian buffer (Conservation Easement) and 0.0168 km^2 of riparian wetland creation, based on the soil assessment of the watershed (Environmental Banc & Exchange, 2013).

The primary goal of the restoration project was to address the water quality degradation, by excluding livestock; restoring the riparian buffer, improving channel stability, wetland hydrology, terrestrial and aquatic diversity and native vegetative community structure. The first and second order streams were divided into a total of six reaches based on their morphological condition and contributing watershed area (Figure 4). The channels in Reaches 1, 2, 3, 5, and 6 were identified to be devolving to the Rosgen ‘Gc’ classification range, characterized by slope less than 0.02 with high entrenchment, low width to depth ratio and moderate sinuosity. These stream features are common in agricultural landscape and the stream displayed rapid channel adjustment (Natural Resources Conservation Service, 2007).

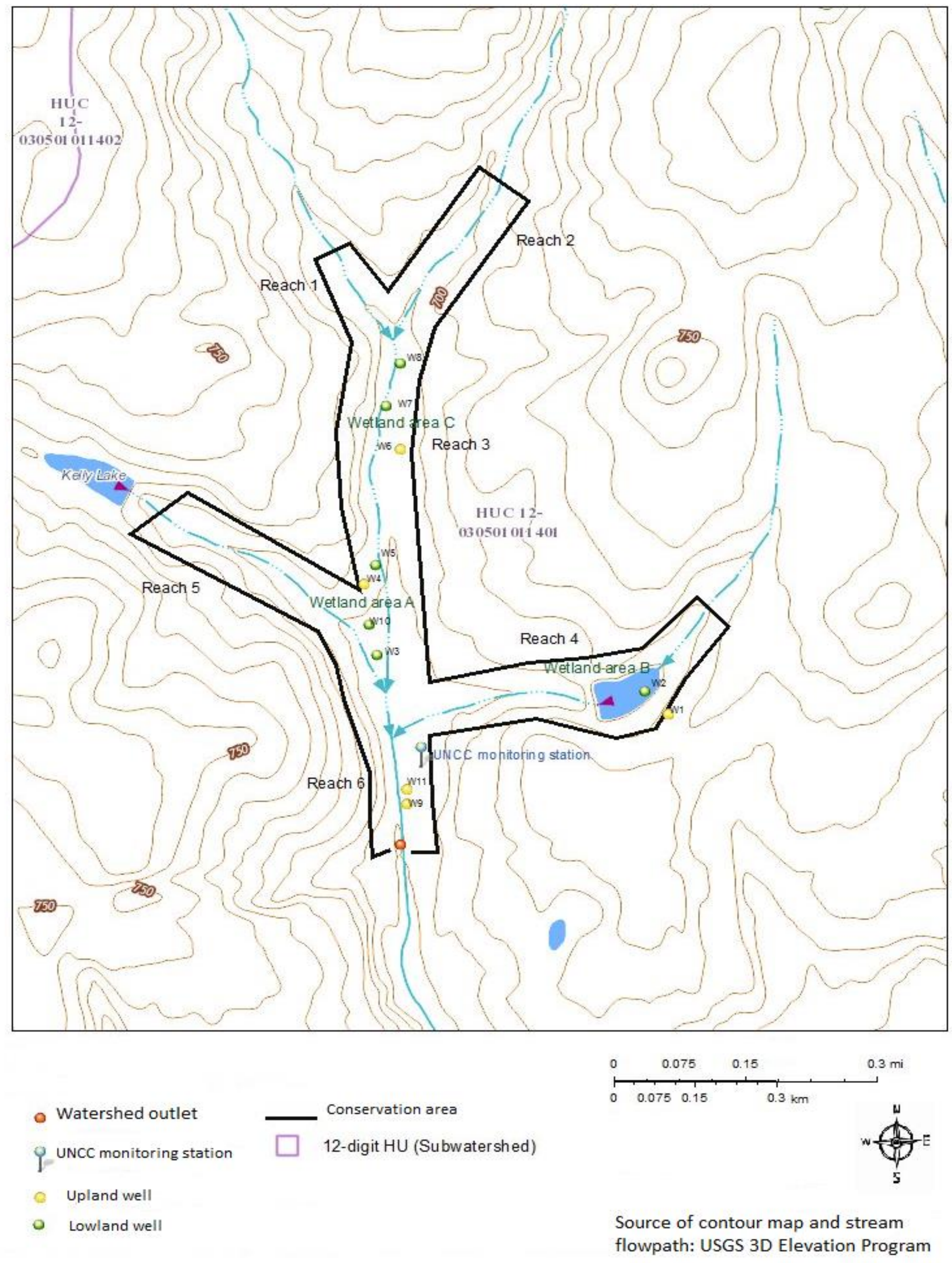


Figure 4: Map of MC5 stream restoration including location of Reaches (1 to 6), Wetlands (A to C), Groundwater monitoring wells (1 to 11), UNCC monitoring station and boundary of conservation area at the MC5 sub-watershed

A Priority 1 restoration (raising the stream bed in the range from 0.914 m (3 feet) to 1.52 m (5 feet)) was performed on Stream Reach 1, 3, 5 sections (Figure 4). The stream restoration, repatterned the stream channel except for Reach 6. Wetland A (0.0108 km^2) was restored between Reach 3 and 5. Wetland B (0.00308 km^2) was originally an impounded livestock pond on Reach 4. Wetland Area C (0.00291 km^2) was created at the beginning of Reach 3. The upper portion of Reach 4 was improved by implementing a Level 1 enhancement. The riparian buffer of 15.2 m (50 feet) width along both the sides of the channel through the length of each reach was set aside as a conservation easement and was fenced to exclude cattle and other livestock from accessing the stream and to accommodate the continued agricultural use of the land area outside the conservation easement.

The hydraulic analysis of the design 100-year rainfall event was performed on each stream reach. The analysis indicated that any increases in the 100 year Water Surface Elevations (WSEs) were contained within the Conservation easement or the design reduced the 100 year flood elevation (Environmental Banc & Exchange, 2012). The vegetation planting plan for the site was implemented to develop an Alluvial Forest Community based on local reference sites and was divided into 3 zones: stream bank, riparian areas, and restored/ created headwaters wetlands.

5.6 Post-restoration monitoring

The restored site is currently being monitored for five consecutive years after the completion of the restoration project to confirm stable channel geomorphology, in-stream structure integrity, and riparian vegetative success. The restored wetlands on the site are being monitored for seven consecutive years to confirm hydrology, vegetation, and soil conditions meet required wetland characteristics. Channel stability monitoring included the establishment of twelve permanent cross sections, which are marked throughout the project site, one at a riffle and the other at a pool at each reach, thus representing 50 percent riffles and 50 percent pools. Eighteen vegetative plots of 0.02 acres each were randomly allocated for monitoring the health of vegetation at the site during consecutive monitoring years. Eleven groundwater gauging wells were installed at the site; four of these are located in Wetland Area A, two are in Wetland Area B, three are sited in Wetland Area C, and the remaining two are found in the lower part of Reach 6 (Figure 4). One of the groundwater gauging wells in each wetland area is paired with an upland well installed for reference purposes. A USGS gaging station was installed on July 30, 2015, at the outlet point of the site and is named as 'USGS 0214265828 McDowell Creek Tributary at SR2131 Near Hicks Crossroads, NC'.

5.7 Suburban development

In March 2015 the Town of Huntersville approved the plan of sub-urban development on the MC5 watershed. The construction plan and sketch were approved in June 2015, indicating the total area of the construction site to be 116.7 acres (47.23 hectares), which is 20.26 % of the total MC5 watershed area. A total of 160 single family homes with different lot sizes are to be constructed on the site. In June 2016, the land clearing in the East of the site initiated for construction work of the residential subdivision (Figure 5).

The suburbanization projects in the Town of Huntersville are to adhere to the Low Impact Development Ordinance (Town of Huntersville, Water Quality Design Manual, 2017), which was passed in 2003, as well as the EPA National Pollutant Discharge Elimination System (NPDES) Phase II Storm Water Quality regulations (EPA 2005). New developments are required to provide storm water management plans, including water quality BMPs. Low Impact Development (LID) is a comprehensive stormwater management approach which aims to maintain and restore a watershed's hydrologic regime by creating landscapes that mimic the natural hydrologic functions of infiltration, runoff and evapotranspiration (Perrin et al., 2009).

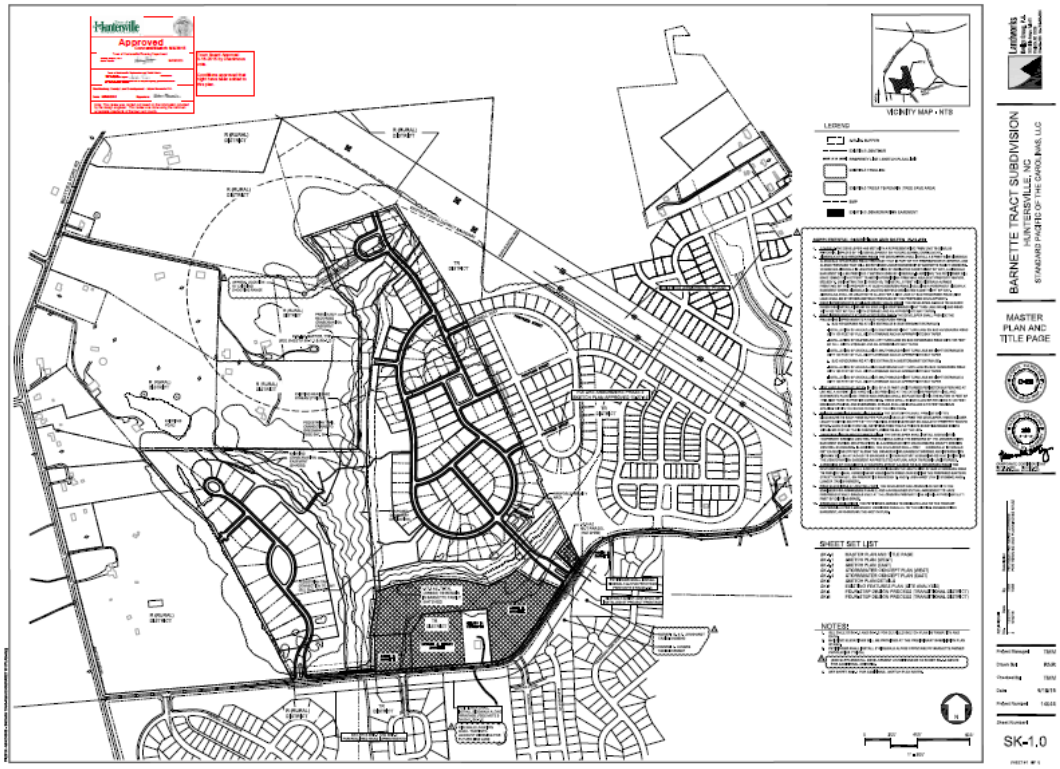


Figure 5: Construction plan at the MC5 study site approved by Town of Huntersville and Mecklenburg County Land Development in June 2015 (Adopted from Landworks Design Group, P.A.)

6. RESULTS AND DISCUSSION

6.1 Hydrology

6.1.1 Water balance

The water balance approach was applied to the hydrologic parameters of two consecutive water years (2016 and 2017) of the study watershed to understand the seasonal dynamics in the dormant and growing seasons. The Table 3 shows the monthly water balance of two dormant seasons (October 2015 to March 2016 and October 2016 to March 2017) and two growing seasons (April 2016 to September 2016 and April 2017 to September 2017). Henceforth, the dormant season from October 1, 2015 to March 31, 2016 is referred to as Dormant Season I (DS-I) and from

October 1, 2016 to March 31, 2017, is referred to as Dormant Season II (DS-II). Similarly, the growing season from April 1, 2016 to September 30, 2016 is referred to as Growing Season I (GS-I) and from April 1, 2017 to September 30, 2017 is referred as Growing Season II (GS-II).

Figure 6 shows the hydrograph and hyetograph from July 30, 2015 to November 2, 2017. Figure 7 shows the flow duration curve depicting the percent exceedance of daily surface runoff for the dormant and growing seasons of water year 2016 and 2017. Table 4 shows the mean, median, 20 % and 80 % probability of exceedance and cumulative daily surface runoff for the dormant and growing seasons of water year 2016 and 2017.

6.1.1.1 Precipitation, surface runoff and runoff coefficient

There was significant precipitation variability between the dormant seasons and growing seasons for both the water years. The precipitation in DS-I was higher by 53% as compared to GS-I, whereas precipitation in DS-II was 51% less than GS-II (Table 3). The surface runoff of GS-I was 77% less as compared to that in DS-I, and it was higher by 35 % in GS-II than DS-II (Table 3). Generally, during the dormant season the active vegetative cover on the land surface is significantly reduced and this leads to higher surface runoff during the dormant season as compared to the growing season. The runoff coefficient was consistently higher for both dormant seasons as compared with its paired growing season. The runoff coefficient was 65 % and 35 % less for growing seasons of water years 2016 and 2017, respectively as compared to the preceding dormant seasons.

The dormant season of water year 2016 had 89% and 87% more precipitation and surface runoff as compared to the dormant season of water year 2017, but both the dormant seasons showed consistency in the runoff coefficient, which was 0.23. The growing season of water year 2017 was the wettest and received 64 % more precipitation than the previous growing season and resulted in 88 % rise in runoff coefficient (Table 3).

Table 3: Monthly water balance of Dormant season (October 2015 to March 2016 and October 2016 to March 2017) and Growing season (April 2016 to September 2016 and April 2017 to September 2017). [P=Precipitation; SR=Surface Runoff; RC=Runoff Coefficient; Est Et=Estimated Evapotranspiration; Pot Et=Potential Evapotranspiration; Est ΔS=Estimated change in storage; Δ SM=Change in Soil Moisture; Δ GW=Change in Ground Water]

Season	Months	P (cm)	SR (cm)	RC	Est Et + Est Δ S = P - SR (cm)	Pot Et (cm)	Est Δ S = P – (SR + Pot Et) (cm)	Δ SM change (cm)	Δ GW change (cm)
Dormant season – I (DS-I)	**October-15**	16.00	0.91	0.06	15.09	11.26	**3.83**	NA	**8.72**
	November-15	23.29	4.68	0.20	18.61	9.62	**8.99**	NA	**12.65**
	December-15	24.87	6.79	0.27	18.08	9.54	**8.54**	NA	**0.01**
	January-16	4.04	1.96	0.49	2.08	10.58	-8.50	NA	-3.04
	February-16	6.05	2.16	0.36	3.88	9.58	-5.70	NA	-0.59
	March-16	3.45	1.21	0.35	2.24	11.78	-9.54	NA	-6.80
Total	**DS-I**	**77.70**	**17.71**	**0.23 ***	**59.98**	**62.36**	**-2.38**	**NA**	**10.95**
Growing season – I (GS-I)	**April-16**	5.44	0.82	0.15	4.62	12.80	-8.18	-1.07	**4.47**
	May-16	14.61	2.01	0.14	12.59	15.19	-2.60	-0.40	-9.10
	June-16	4.65	0.33	0.07	4.32	17.57	-13.25	**0.21**	-1.67
	July-16	8.66	0.19	0.02	8.47	19.23	-10.76	-1.05	-12.31
	August-16	3.89	0.02	0.00	3.87	18.04	-14.17	-1.02	-7.98
	September-16	13.64	0.74	0.05	12.9	14.58	-1.69	**1.10**	**17.98**
Total	**GS-I**	**50.89**	**4.11**	**0.08 ***	**46.77**	**97.41**	**-50.65**	**-2.23**	**-8.61**
Dormant season –II (DS-II)	**October-16**	7.62	0.91	0.12	6.71	11.66	-4.95	-0.39	NA
	November-16	2.87	0.20	0.07	2.67	9.58	-6.90	**0.59**	NA
	December-16	6.15	0.76	0.12	5.39	9.58	-4.19	**0.25**	NA
	January-17	13.36	4.71	0.35	8.65	9.65	-1.00	**0.20**	NA
	February-17	2.18	1.22	0.56	0.96	9.47	-8.50	**0.07**	NA
	March-17	8.86	1.64	0.18	7.22	11.45	-4.22	**0.36**	NA
Total	**DS-II**	**41.04**	**9.44**	**0.23 ***	**31.6**	**61.39**	**-29.76**	**1.08**	**NA**
Growing season – II (GS-II)	**April-17**	14.96	2.79	0.19	12.17	13.27	-1.10	**0.15**	NA
	May-17	19.71	2.41	0.12	17.31	15.46	**1.85**	**0.02**	NA
	June-17	13.31	1.30	0.10	12.01	16.87	-4.86	-0.86	NA
	July-17	7.59	0.98	0.13	6.62	18.74	-12.12	-2.55	NA
	August-17	13.18	0.77	0.06	12.41	16.76	-4.35	**0.74**	NA
	September-17	14.88	4.54	0.31	10.34	13.67	-3.33	-1.80	NA
Total	**GS-II**	**83.63**	**12.79**	**0.15 ***	**70.86**	**94.77**	**-23.91**	**-4.30**	**NA**

[* RC = SR/P]

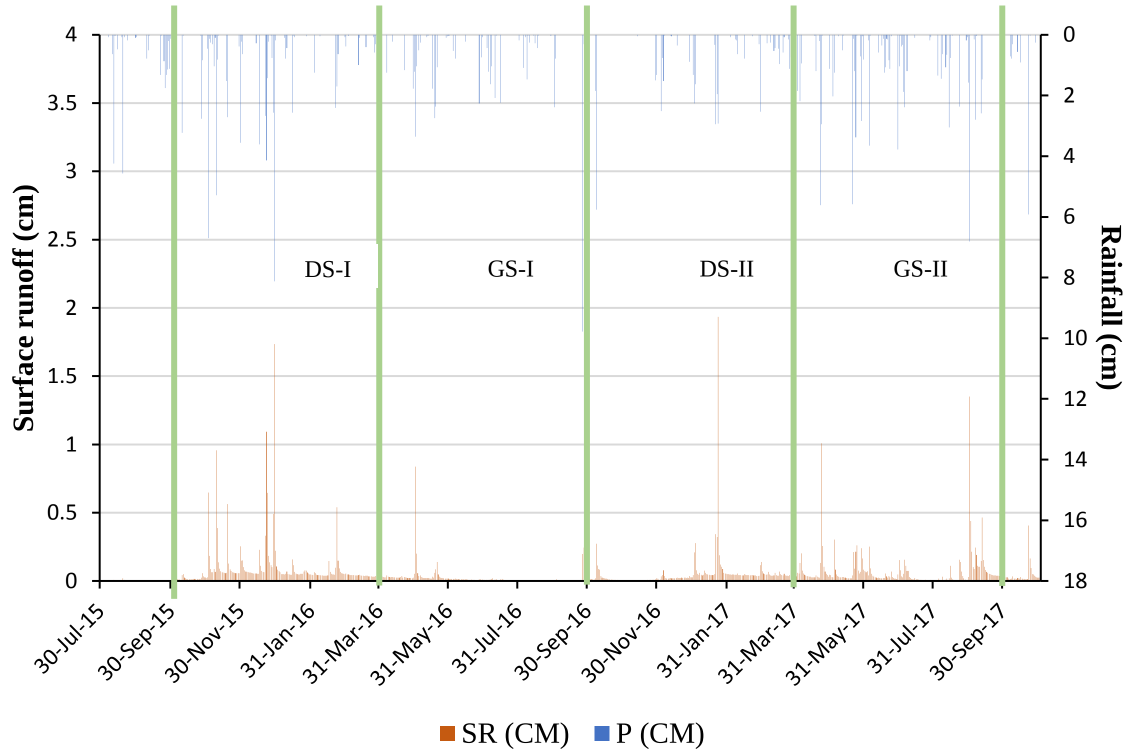


Figure 6: Hydrograph and Hyetograph from July 30, 2015 to November 2, 2017 (green bar demarcating the seasons)

As seen in Figure 7, the surface runoff for both the dormant and growing seasons showed similar trend (overlap) for the percent of high flow runoff events (5 – 15 %). There was a difference in the first five percent of the high runoff events, but for flow period greater than equal to 85%, the two seasons diverged in runoff trends. As seen in Table 4, the cumulative surface runoff for growing season was 38 % less than that of the dormant season and for 80 percent exceedance the growing season surface runoff was 76 % less than that in the dormant season. The difference in the two seasons for runoff events with an 85 percent probability can be attributed to higher evapotranspiration during growing season. This leads to a declining trend in surface runoff as compared to the dormant season, whereas during the dormant season the stream channel is continuously recharged with shallower ground water, leading to a more constant flow in the stream channel.

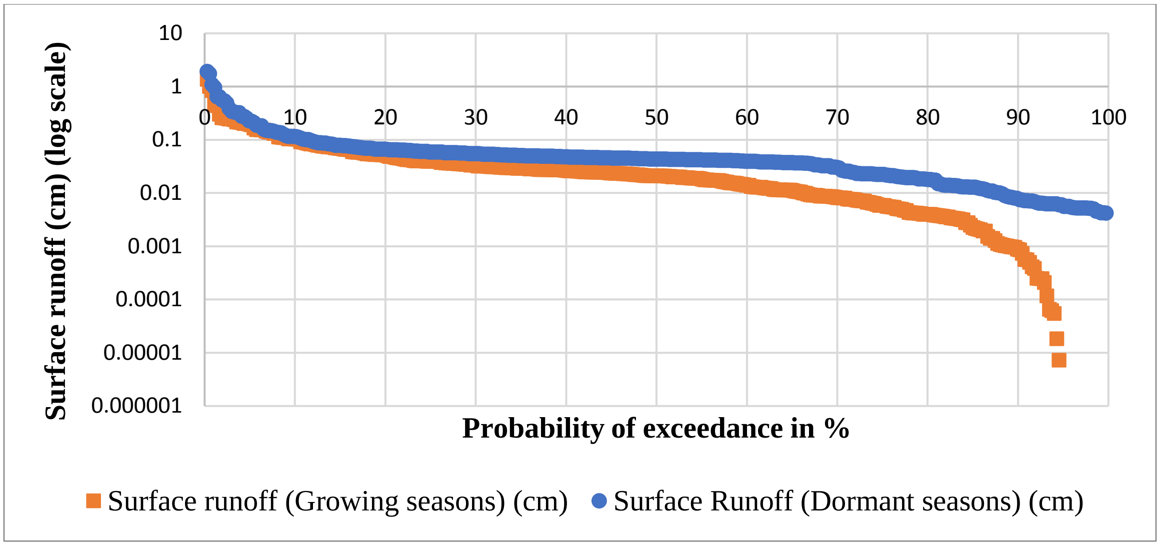


Figure 7: Flow duration curve showing the percent exceedance of daily surface runoff for the dormant and growing seasons of water year 2016 and 2017

Table 4: Mean, median and probability of exceedance of daily surface runoff for the dormant and growing seasons of water year 2016 and 2017

Surface runoff (cm)	Mean	Median	20% exceedance	80% exceedance	Cumulative surface runoff (cm)
All period	0.060	0.032	0.058	0.010	45.62
Dormant season	0.074	0.043	0.066	0.017	27.16
Growing season	0.046	0.021	0.050	0.004	16.90

6.1.1.2 Evapotranspiration and change in storage

In this water balance study, the difference between the precipitation and surface runoff is used to understand the evapotranspiration and change in storage. The monthly potential evapotranspiration as estimated using the Thornthwaite equation, shows GS-I potential evapotranspiration more than 56 % than DS-I and GS-II potential evapotranspiration more than 54 % compared to DS-II (Table 3). The atmospheric air temperature of DS-I was 53 % lower than GS-I and DS-II was 50 % lower than GS-II; and the long term normal air temperature data shows that dormant season air temperature is typically 59 % less than the growing season temperature (Table 2). Thus, during the dormant season when the atmospheric temperatures are low and the vegetation is sparse and biologically inactive, the evapotranspiration is significantly lower. The actual evapotranspiration is generally less than the potential evapotranspiration for the corresponding period because the later assumes unlimited availability of surface water, which is not the case in natural conditions. The trend of significantly higher potential evapotranspiration during the growing seasons as compared to the dormant seasons is indicative of corresponding trend in actual evapotranspiration. Therefore, the difference between precipitation and surface runoff, will have a greater evapotranspiration component in the growing season, as supported by the consistently higher potential evapotranspiration component in the growing seasons by 55 % greater as compared to the preceding dormant seasons. Field measurements of soil moisture and shallow ground water levels, both display deficits in the growing season, whereas the groundwater level change shows a surplus in dormant season (Table 3). The higher evapotranspiration during the growing season in the study site lead to lower soil moisture and shallow groundwater levels as compared to the dormant season, when the vegetation growth and activity are diminished with lower air temperature and leaf senescence.

In the literature, studies have used the difference in precipitation and runoff as the amount of evapotranspiration, assuming change in storage to be zero (Boggs et al. 2013; Boggs and Sun 2011). Following this method, the overall evapotranspiration percentage with respect to precipitation was 83 % and 82 % for water year 2016 and 2017, respectively for the MC5 watershed. Using this approach average evapotranspiration of Beaverdam Creek for the period 2006 to 2012 was 83% of precipitation. Studies conducted in the forested Piedmont watersheds have shown evapotranspiration to range from 78 % to 85 % (Boggs et al. 2013). In this study the seasonal analysis showed percentage of evapotranspiration to precipitation for growing season ranged from 85 % to 92 %, but the dormant season evapotranspiration showed consistency for both the water years 2016 and 2017, to be 77 %. The Hubbard Brook Experimental Forest, Watershed 1, with 100 % forest land cover showed mean evapotranspiration percentage to precipitation to be 87 % for the growing season and 57 % for the dormant season (Sopper & Lull, 1965, 1970).

6.2 Surface water quality and hydrochemical transport

The data of all the 301 outlet water samples for the 27 water quality constituents was tested for normality and then tested for statistical difference between the 4 groups, namely DSBF, DSHF, GSBF and GSHF, as discussed in the methods section. After the log transformation, all but one water quality constituent showed significant deviation from the normal distribution. The one water quality constituent which showed normal distribution ($p > 0.05$) was PO_4^{3-} ion concentration (Table 5). The Kruskal Wallis H test (non-parametric equivalent of one-way ANOVA) was performed on the four groups, namely GSBF, GSHF, DSBF and DSHF, and the results for significance value is shown in Table 5. All the water quality constituents, but one show significant difference between the four groups ($p < 0.05$). For TDP concentration the significance value was greater than 0.05, suggesting no significant difference between the different season and flow type. The parametric test, one-way analysis of variance was run for PO_4^{3-} ion concentration, and it gave $p > 0.05$, implying no significance difference between the four groups for this water quality constituent.

The Kruskal-Wallis post-hoc test was performed to identity pairwise significant differences between the groups. The Growing Season Base Flow (GSBF) was compared with Dormant Season Base Flow (DSBF) (Comparison 1) and with Growing Season High Flow (GSHF) (Comparison 2), respectively. Similarly, the Dormant Season High Flow (DSHF) was compared to Dormant Season Base Flow (DSBF) (Comparison 3) and with Growing Season High Flow (GSHF) (Comparison 4), respectively. The results of the post-hoc tests are presented in the Tables 8, 11, 14, 17, 20 and 21.

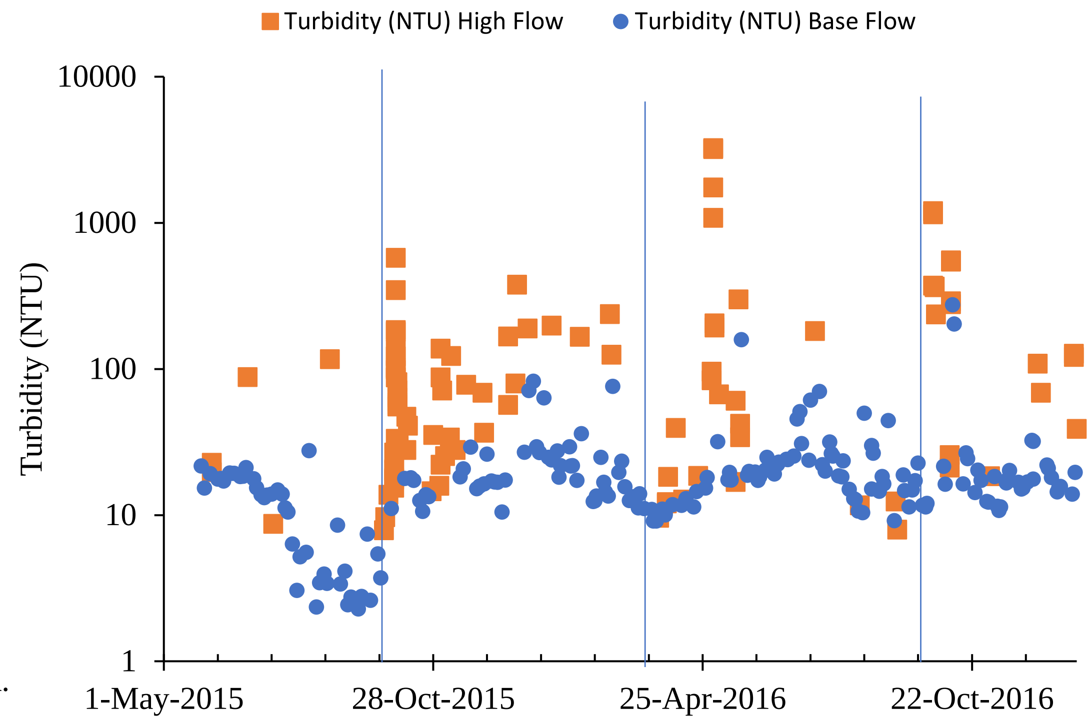
Table 5: Normality test (before and after log transformation) and Non-Parametric One-Way analysis of variance (Kruskal Wallis H test) for the water quality constituents (Significance level is 0.05) (Note: One-way ANOVA for PO_4^{3-} concentrations)

Water quality constituents		n	p value after Shapiro Wilk test (Test of Normality)	p value after log transformation and Shapiro Wilk test (Test of Normality)	p value after One-Way ANOVA (Parametric/Non-parametric) between four groups
Probe measurement	Conductivity	301	0.000	0.000	0.000
	Turbidity	299	0.000	0.000	0.000
Sediments	TSS	300	0.000	0.000	0.000
Carbon	TOC	301	0.000	0.000	0.000
	DOC	300	0.000	0.000	0.000
	POC	301	0.000	0.000	0.001
Nitrogen	TN	300	0.000	0.001	0.000
	TDN	300	0.000	0.002	0.000
	PN	301	0.000	0.043	0.000
	DON	301	0.000	0.000	0.025
	NH_4^+	301	0.000	0.001	0.003
	NO_3^-	301	0.000	0.000	0.000
Phosphorous	TP	297	0.000	0.000	0.006
	TDP	300	0.000	0.000	**0.095**
	PP	301	0.000	0.001	0.001
	DOP	301	0.000	0.000	0.000
	PO_4^{3-}	301	0.000	**0.279**	**0.113**
Cations	H^+	299	0.000	0.000	0.000
	Na^+	301	0.000	0.000	0.000
	K^+	301	0.000	0.000	0.000
	Ca^{2+}	301	0.000	0.000	0.000
	Mg^{2+}	301	0.000	0.000	0.000
Anions	F^-	301	0.000	0.000	0.000
	Cl^-	301	0.000	0.000	0.000
	Br^-	301	0.000	0.000	0.000
	SO_4^{2-}	301	0.000	0.000	0.000
	HCO_3^-	301	0.000	0.000	0.000

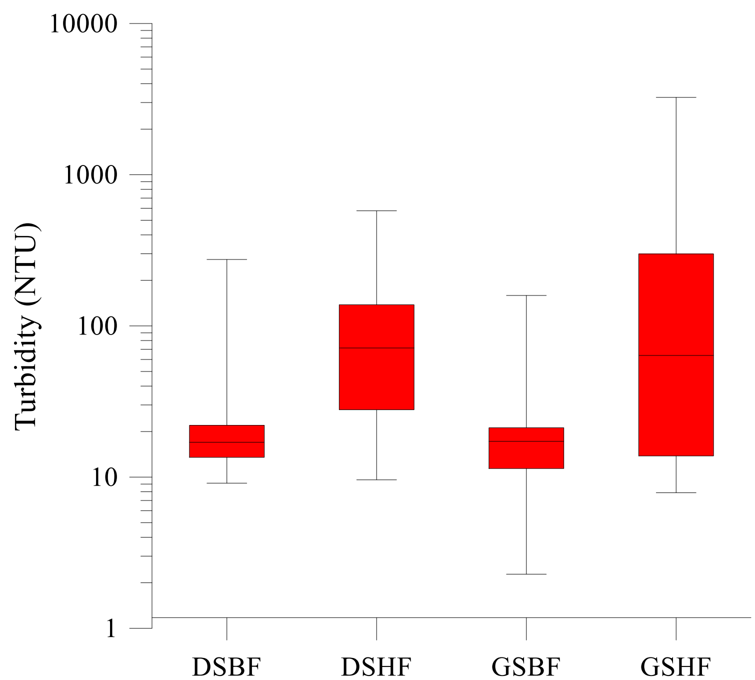
6.2.1 Turbidity and Total Suspended Sediments

Both turbidity and TSS concentrations showed flow specific trends, that is the high flow samples had consistently higher turbidity and TSS concentrations than the base flow samples, irrespective of specific season (Figure 8 and 9). This is supported statistically (Table 6 and Figure 8 B), as turbidity of growing season high flow and the dormant season high flow was significantly higher than the base flow of the respective seasons. Similarly, the TSS concentration of growing season high flow and dormant season high flow was higher by an order of magnitude than the base flows of the respective seasons (Figure 9 B). This indicates that the surface runoff generated by the precipitation during the high flow events is the agent of significantly higher concentration of suspended solids and hence turbidity of stream water.

The hydrochemical transport of TSS yield (kg/ha/cm) increased by 15% in the growing season of water year 2016 as compared to the dormant season of water year 2016 (Table 7). The turbidity of the growing season was approximately 5 times higher as compared to the dormant season of water year 2016 (Table 6). The precipitation during growing season of water year 2016 was 35% less as compared to that during dormant season of water year 2016 (Table 3). Thus, the significantly higher of TSS and volume weighted average for turbidity during the growing season as compared to the dormant season of water year 2016, is indicative of the initiation of the land use change and active construction activity in the eastern region of the watershed (Figure 12, 13, 14). As per field observations, the construction activity was initiated in March 2016.



A.



B.

Figure 8: (A.) Scatter plot of MC5 stream's turbidity from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's turbidity from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF (Note: Y-axis of both plots are in log scale)

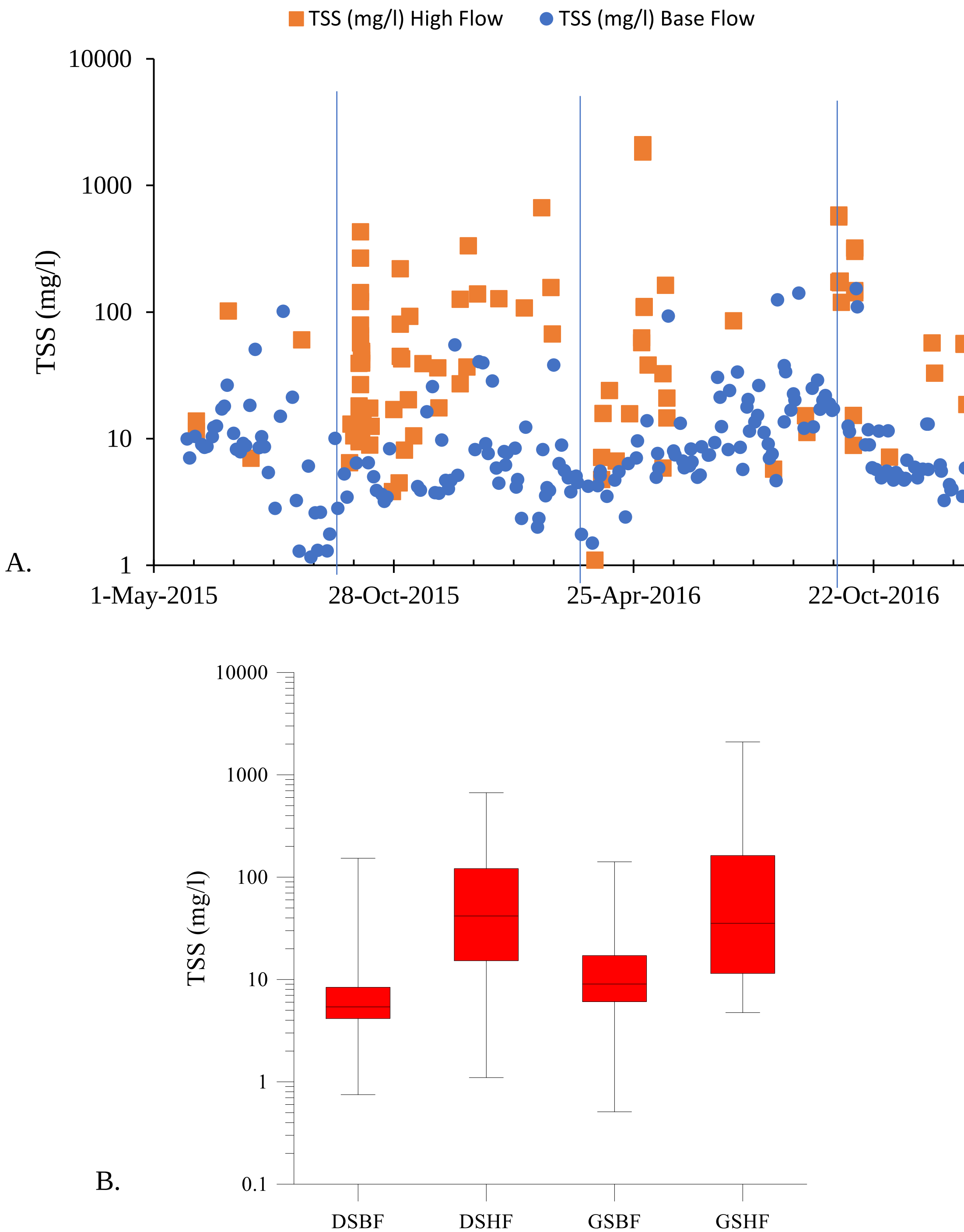


Figure 9: (A.) Scatter plot of MC5 stream's TSS concentration from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's TSS concentration from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF (Note: Y-axis of both plots are in log scale)

Table 6: Volume weighted average of MC5 stream's turbidity for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituents (by probe measurement)	Volume Weighted Average	
	Dormant season	Growing season
Turbidity	135.76 ± 13.96	637.47 ± 88.44

Table 7: Hydrochemical transport of MC5 watershed's TSS for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituents	Dormant season			Growing season		
	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)
TSS	53,743.89 ± 5,413.15	230.660 ± 23.232	2.9686 ± 0.2990	40,288.94 ± 5,328.40	172.914 ± 22.869	3.3985 ± 0.4495

Table 8: Kruskal-Wallis post hoc test, showing pair-wise significant differences between DSBF, DSHF, GSBF and GSHF of MC5 stream's turbidity and TSS concentrations from May 26, 2015 to December 31, 2016 ($p = .05$)

Water quality constituents	GSBF – DSBF (Comparison 1)	GSBF – GSHF (Comparison 2)	DSBF – DSHF (Comparison 3)	GSHF – DSHF (Comparison 4)
Turbidity	1.000	0.000	0.000	0.309
TSS	0.001	0.000	0.000	1.000

The discharge and TSS linear regression relationship showed a positive correlation with 84% of variation in TSS explained by the change in discharge (Figure 11Ai). The linear regression between discharge and turbidity also showed positive correlation between the two variables and 72% of variation in turbidity can be explained with the change in discharge (Figure 11 Bi). Thus, the linear regression between turbidity and TSS also showed a positive correlation and 89% of variations in TSS was explained by the change in turbidity for the grab water samples collected from July 31, 2015 to December 31, 2016 (Figure 10). Sediment surrogate techniques using turbidity and discharge to estimate suspended sediment concentrations gave R square of 81.1% and

92.7% for streams in Washington (Uhrich et al., 2014). Further, the sediment transport rating relationship between discharge and TSS of MC5 stream for the period from July 31, 2015 to December 31, 2016 (Figure 11Aii), showed 61.5% less sediment load carried in the MC5 stream under low flow conditions and 64.3% lower rate of change of TSS concentration with respect to change in discharge, as compared to the BD1 stream for the time period 2003 to 2012 ($y = 709.88\ x^{1.6929}$) (Allan et al., 2013).

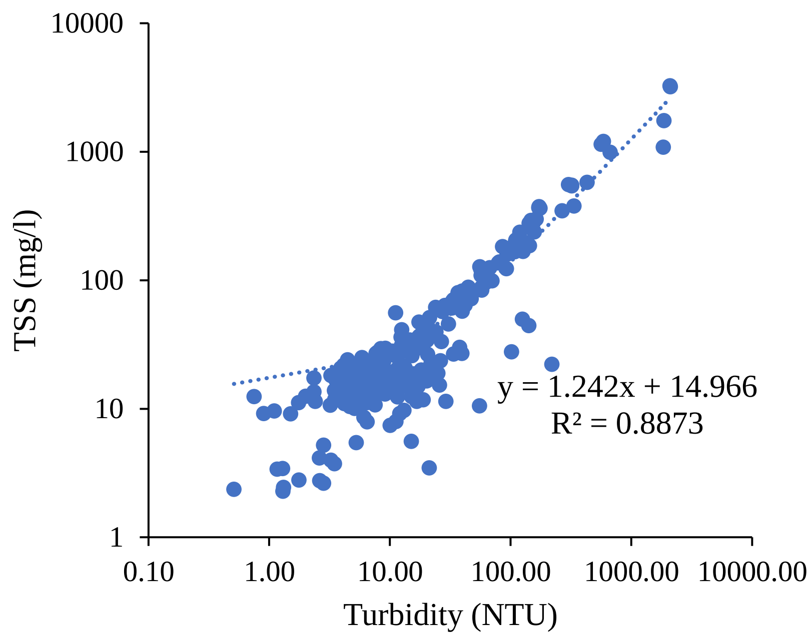


Figure 10: Linear regression relationship between turbidity and TSS (both in log scale) for MC5 stream from July 31, 2015 to December 31, 2016

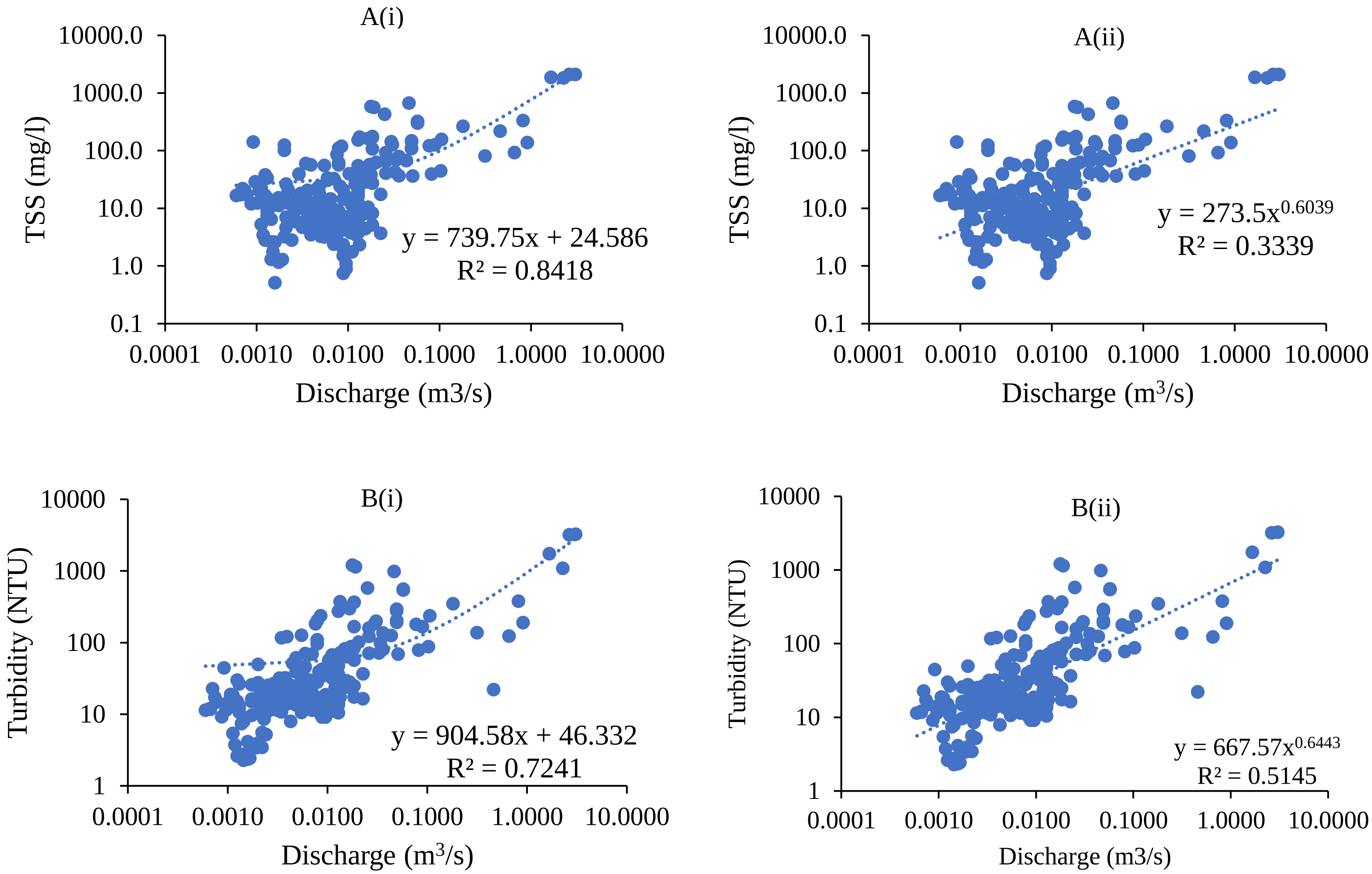


Figure 11: Regression relationship between (A.) Discharge and TSS - (i) linear equation, (ii) power equation; (B.) Discharge and Turbidity - (i) linear equation, (ii) power equation, (all axis in log scale) for MC5 stream from July 31, 2015 to December 31, 2016

Figure 12: Land clearing in the eastern region of the MC5 watershed near Tributary East (Photograph taken on July 9, 2016 at 8:45 am)

Figure 13: Installation of stromwater infrastructure in the eastern region of the MC5 watershed near Tributary East (Photograph taken on October 16, 2016 at 5:14 pm)

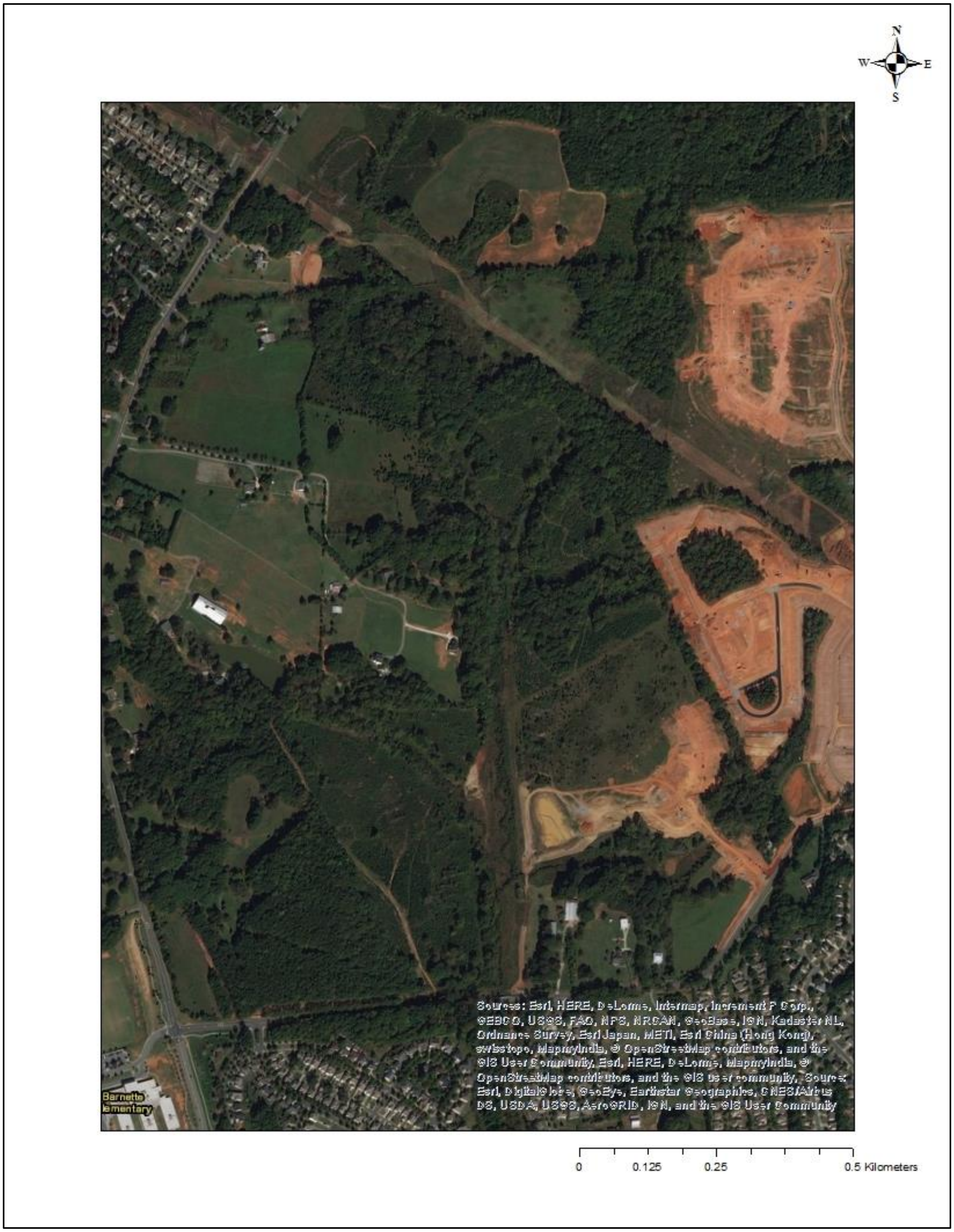


Figure 14: Imagery of the MC5 watershed as on October 25, 2016 (Source: ESRI). (Note: Seen in the photograph is the land clearing in the eastern region of the watershed, the stormwater retention pond and the inroad to the site through the Tributary East.)

6.2.2 Specific conductance, bicarbonate ion (HCO_3^-) and cations (Na^+, Ca^{2+}, Mg^{2+}, K^+, H^+)

Specific conductance showed specific seasonal trends, with a prominent rise in conductivity during the end of growing seasons, as seen in two consecutive water years 2015 and 2016 (Figure 16A). The average base flow conductivity was approximately 100 µS/cm, but reached a peak towards the end of growing season rising to approximately 200 µS/cm (Figure 16 A). Further, the high flow conductivity values were significantly less than the base flow conductivity values for the corresponding time period, whereas there was no significant difference in the high flow conductivity between seasons (Figure 16 B and Table 11). The mean growing season base flow conductivity was significantly higher as compared to dormant season base flow and growing season high flow conductivity by 26% and 44% respectively.

The linear regression between discharge and specific conductance displayed negative correlation (slope = -42.94) with only 11% of variation in conductivity explained by the change in discharge for the grab water sample conductivity and discharge data collected from May 26, 2015 to December 31, 2016 ($y = -42.94x + 116.5$; $R^2 = 0.1131$). Further, it is an indication of dilution of the major ions leading to lower conductivity values during the high discharge events. The power relationship between discharge and conductivity as shown in Figure 15 explained 60% of the variation in conductivity with respect to discharge.

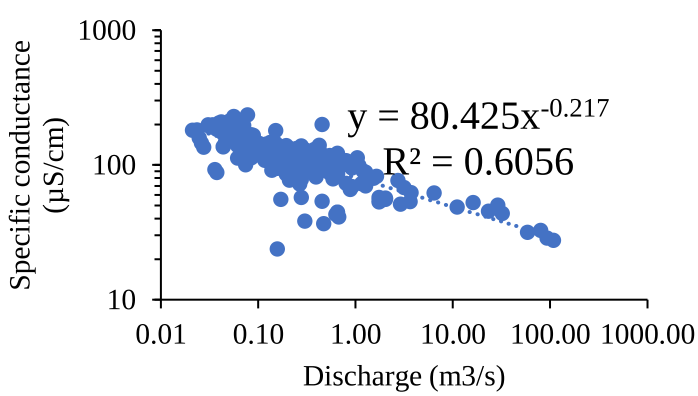
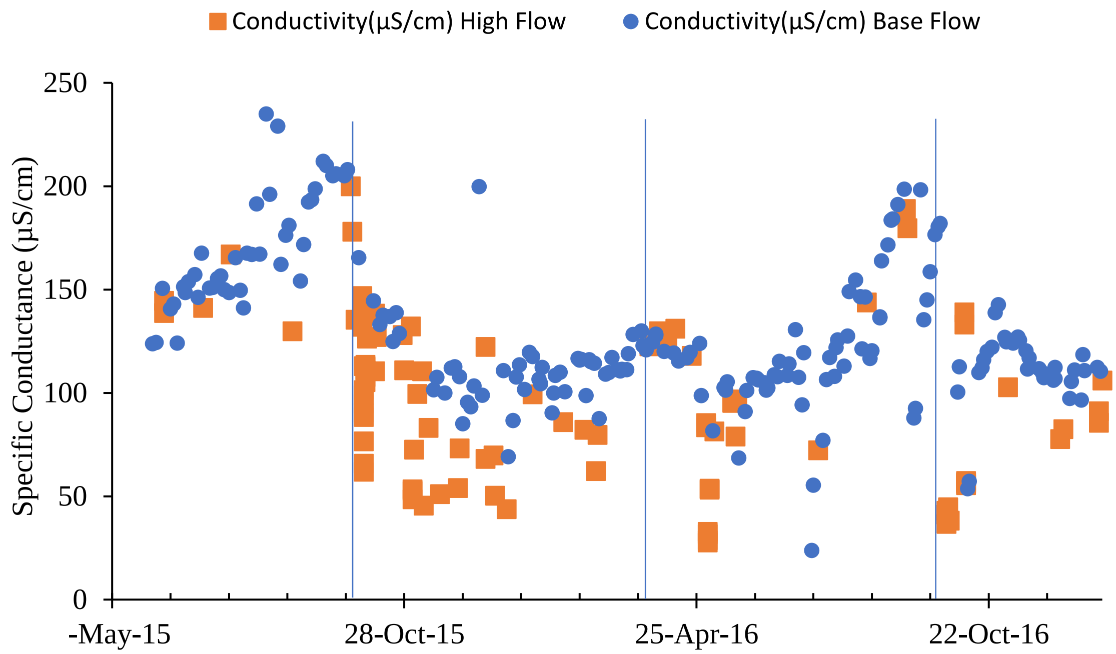
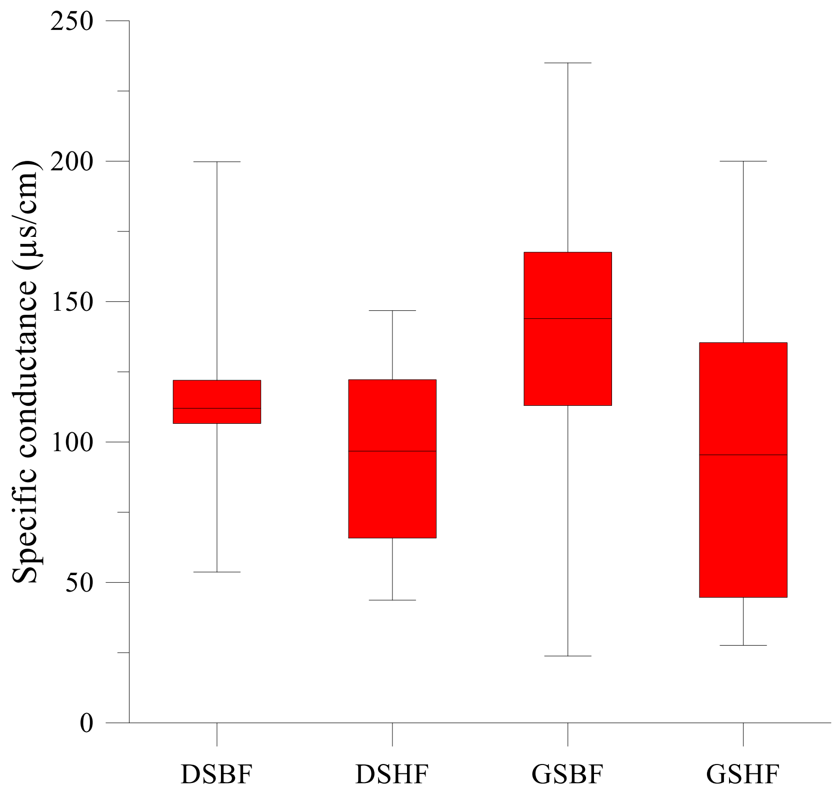


Figure 15: Regression relationship between discharge and specific conductance (both in log scale), with best-fit power trendline for MC5 stream from July 31, 2015 to December 31, 2016



A.

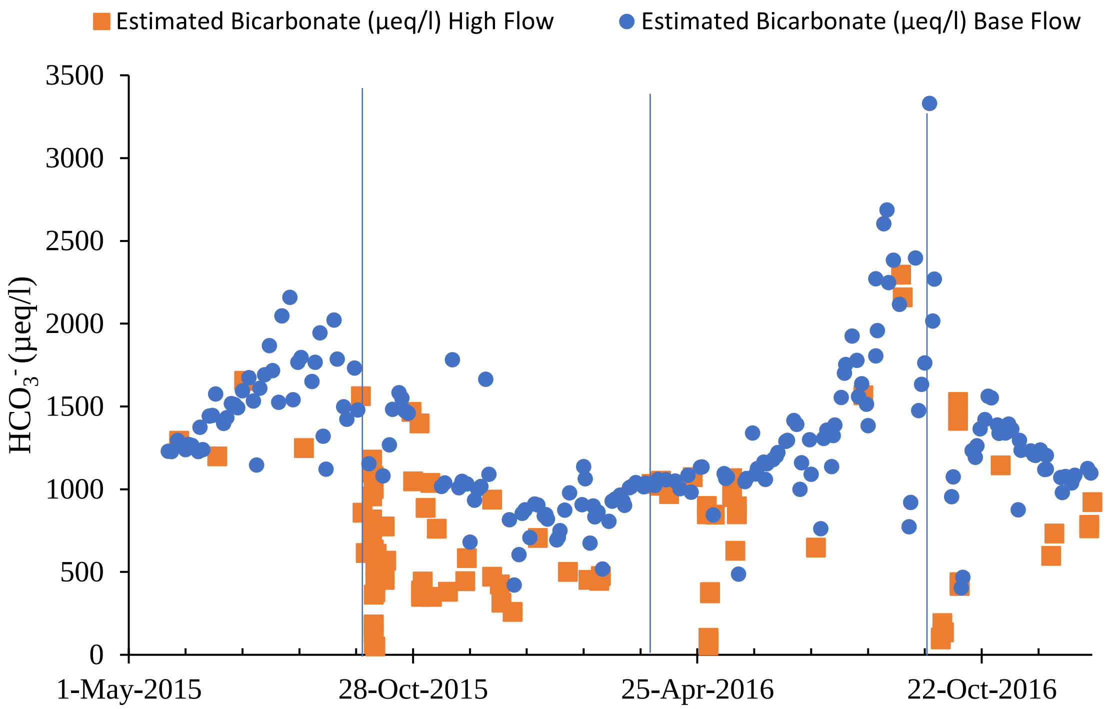


B.

Figure 16: (A.) Scatter plot of MC5 stream's specific conductance from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's specific conductance from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

Estimated HCO_3^- concentrations showed similar seasonal trend as seen in specific conductance, with peaks toward the end of each growing seasons, as seen in two consecutive water years 2015 and 2016 (Figure 17). The average base flow bicarbonate concentration was approximately 1000 μeq/l, but reached a peak towards the end of growing season to approximately 3000 μeq/l as determined from charge balance calculations (Figure 17 A).

The Na^+, Ca^{2+} and Mg^{2+} ion concentrations showed similar seasonal trends as seen in specific conductance and bicarbonate concentrations, with significantly higher concentrations in the growing season base flow stream water samples as compared to the dormant season base flow and growing season high flow water samples (Figures 18, 19, 20). The average base flow Na^+, Ca^{2+} and Mg^{2+} ion concentrations was approximately 7 mg/l, 10 mg/l and 4 mg/l, respectively, but reached a peak towards the end of growing season rising to approximately 12 mg/l, 35 mg/l and 10 mg/l, respectively (Figure 18A, 19A, 20A). All these trends are indicative of the recharge of the MC5 stream by groundwater during the growing season, with deeper longer residence time groundwater recharging the stream towards the end of the growing season (as seen by the distinct peaks of these water quality constituents during the end of the two-consecutive growing season). The dormant season ground water levels were on average 0.4 meters higher than the growing season ground water levels of water year 2015 and 2016.



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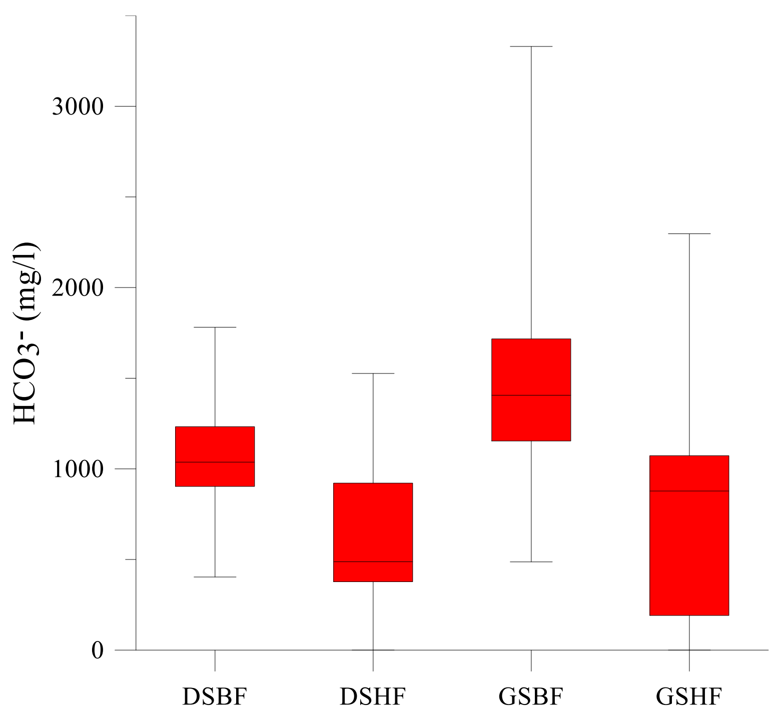
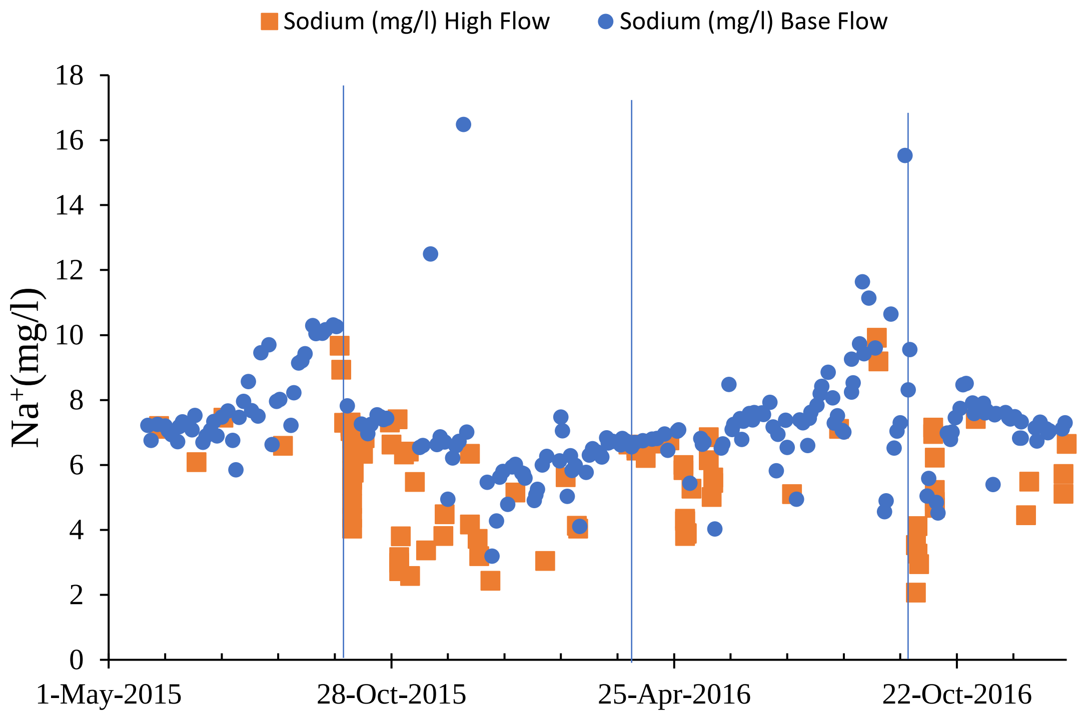


B.

Figure 17: (A.) Scatter plot of MC5 stream's HCO_3^- concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's HCO_3^- concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

A.



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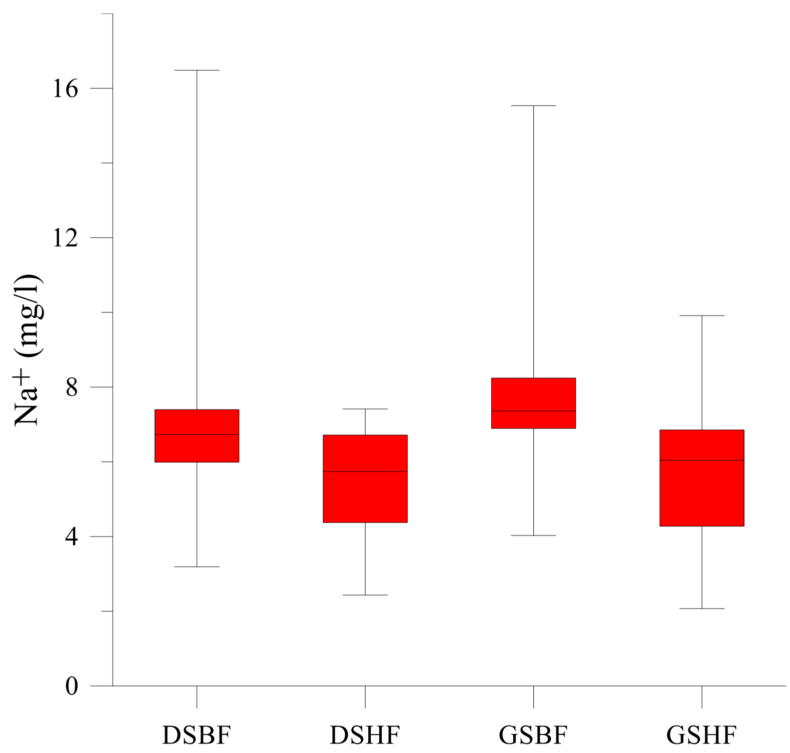
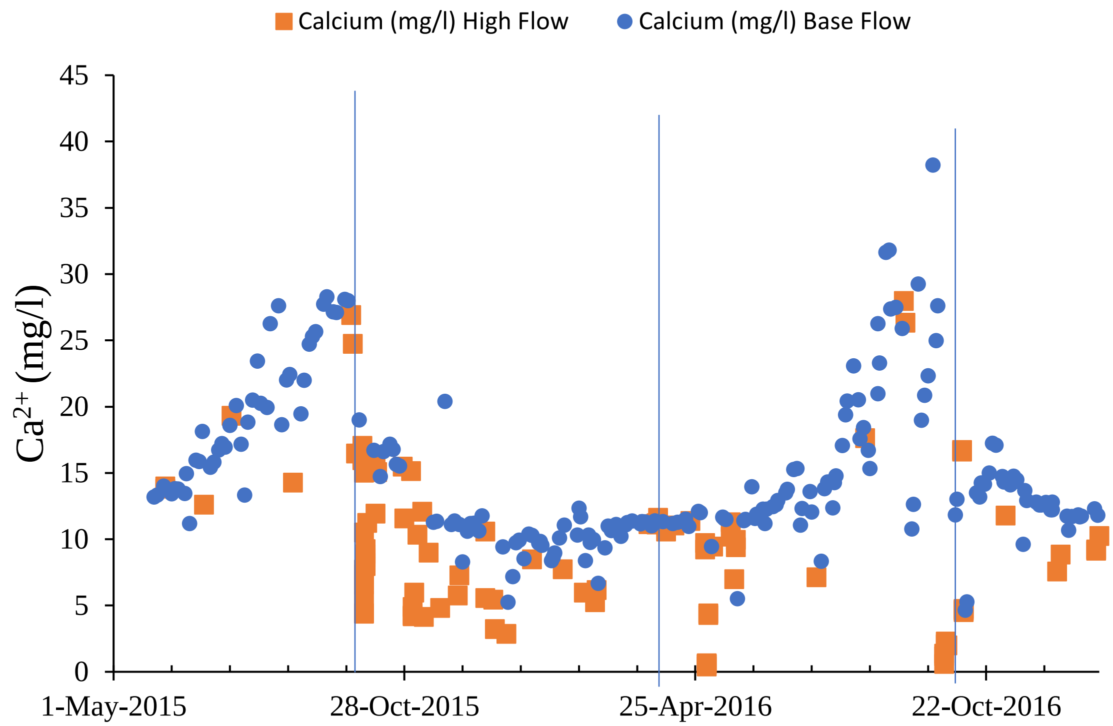
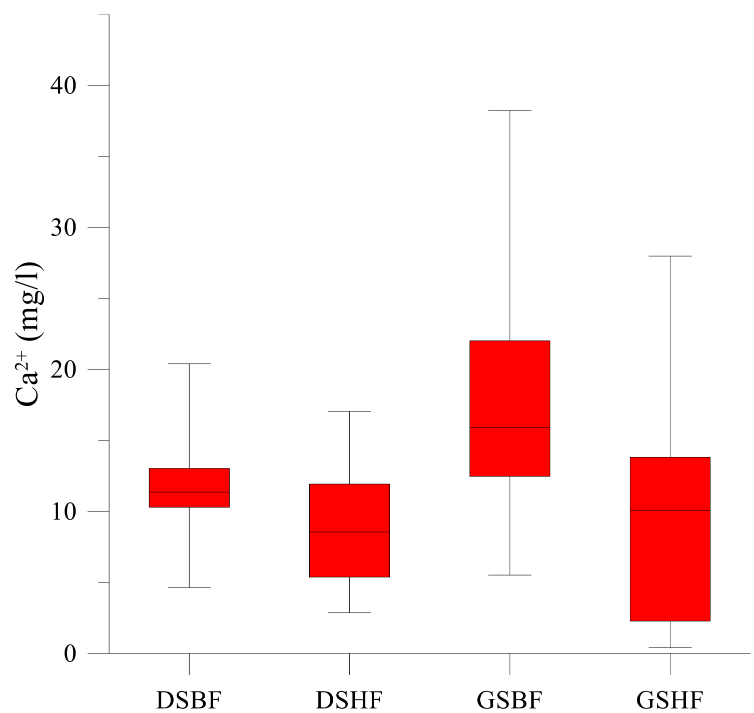


Figure 18: (A.) Scatter plot of MC5 stream's Na^+ concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's Na^+ concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF



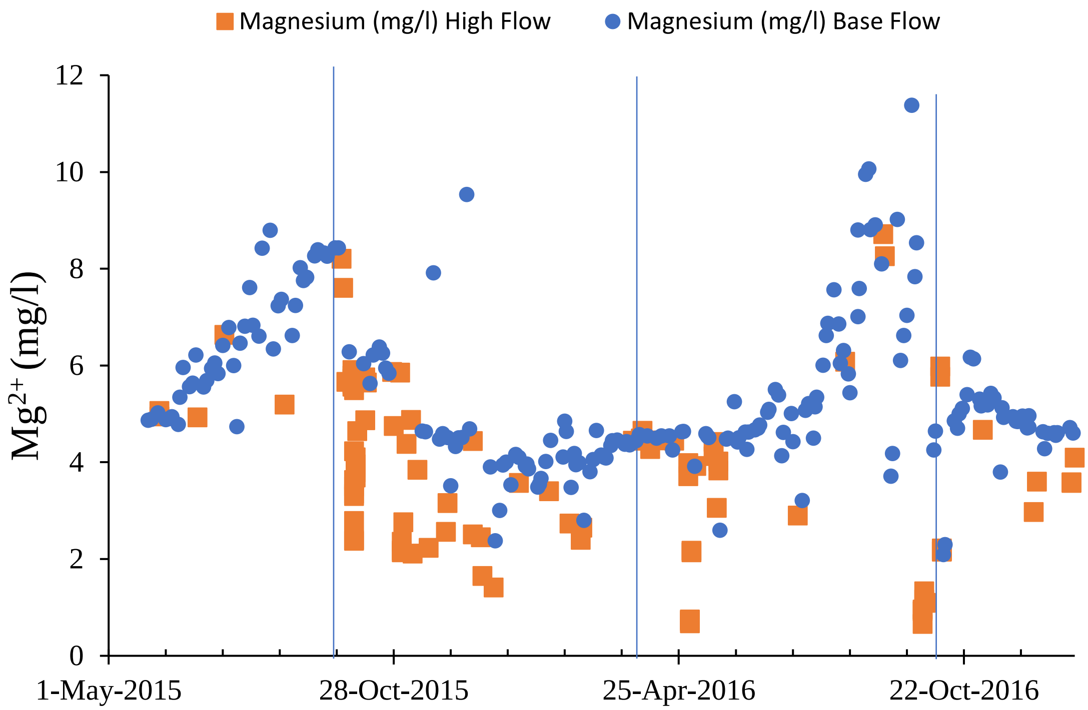
A.



B.

Figure 19: (A.) Scatter plot of MC5 stream's Ca^{2+} concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's Ca^{2+} concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

A.



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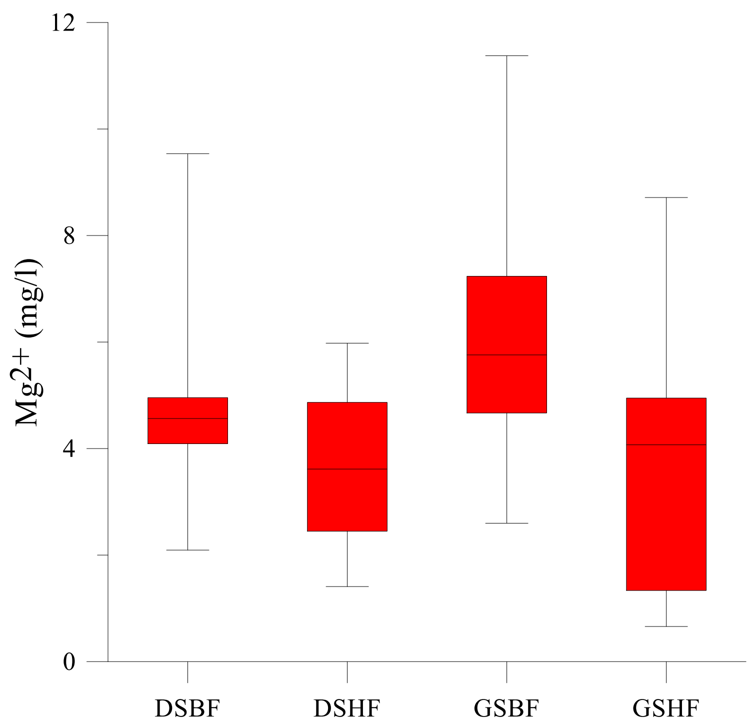


Figure 20: (A.) Scatter plot of MC5 stream's Mg^{2+} concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's Mg^{2+} concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

The volume weighted average of growing season conductivity was 86.05 µS/cm (± 1.59) and that of dormant season was 69.16 µS/cm (± 3.86) for the water year 2016. Thus, the growing season conductivity was 1.24 times more than the dormant season conductivity. Though the volume weighted average of conductivity was significantly higher in the growing season as compared to the dormant season of water year 2016, the overall yield (kg/ha/cm) of HCO_3^-, Na^+, Ca^{2+} and Mg^{2+} ion concentrations from the MC5 watershed in the dormant season was higher by 44%, 59%, 57% and 62% respectively, as compared to the growing season of water year 2016 (Table 9). This is explained by the 77% lesser runoff in the growing season as compared to the dormant season of water year 2016 (Table 3); reduced vegetative uptake during the dormant season as well as the supply of these micro-nutrients by the decomposing litterfall. The mass balance analysis of the growing season of water year 2016 showed 33.53 times, 13 times and 0.6 times higher net export of Ca^{2+}, Mg^{2+} and HCO_3^- ions respectively, as compared to atmospheric inputs (Table 10).

Table 9: Hydrochemical transport of MC5 watershed's HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, K^+ and H^+ for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituents	Dormant season			Growing season		
	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)
HCO_3^-	3,331.27 ± 65.79	14.300 ± 0.282	0.1800 ± 0.0036	1,156.48 ± 5.92	4.960 ± 0.025	0.1000 ± 0.0005
Na^+	2,036.44 ± 114.12	8.740 ± 0.49	0.1125 ± 0.0063	544.61 ± 13.32	2.337 ± 0.057	0.0459 ± 0.0011
Ca^{2+}	3,015.08 ± 145.77	12.940 ± 0.626	0.1665 ± 0.0081	839.67 ± 12.76	3.604 ± 0.055	0.0708 ± 0.0011
Mg^{2+}	1,325.71 ± 67.90	5.690 ± 0.291	0.0732 ± 0.0038	331.10 ± 5.29	1.421 ± 0.023	0.0279 ± 0.0004
K +	1,298.24 ± 98.71	5.572 ± 0.424	0.0717 ± 0.0055	169.04 ± 3.94	0.726 ± 0.017	0.0143 ± 0.0003
H +	256.00 ± 17.59 *	1.099 ± 0.075 **	0.0141 ± 0.0010 ***	50.05 ± 4.46 *	0.215 ± 0.019 **	0.0042 ± 0.0004 ***

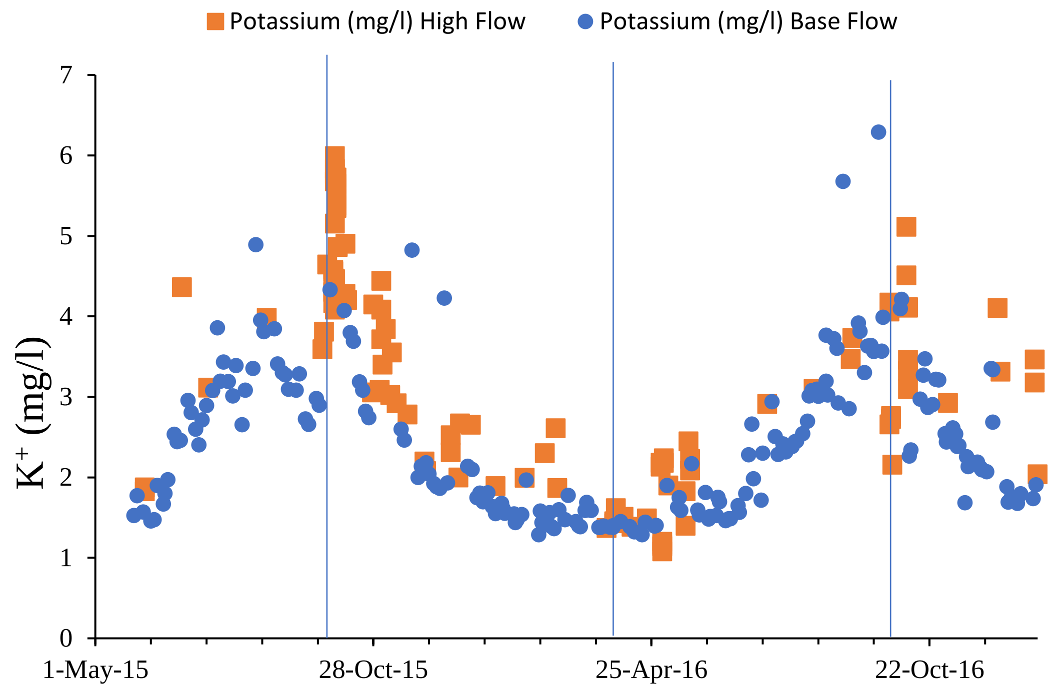
* equivalents, ** eq/ha, *** eq/ha/cm

Table 10: Mass balance of MC5 watershed's HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, K^+ and H^+ for the growing season of water year 2016 (April 1, 2016 to September 31, 2016)

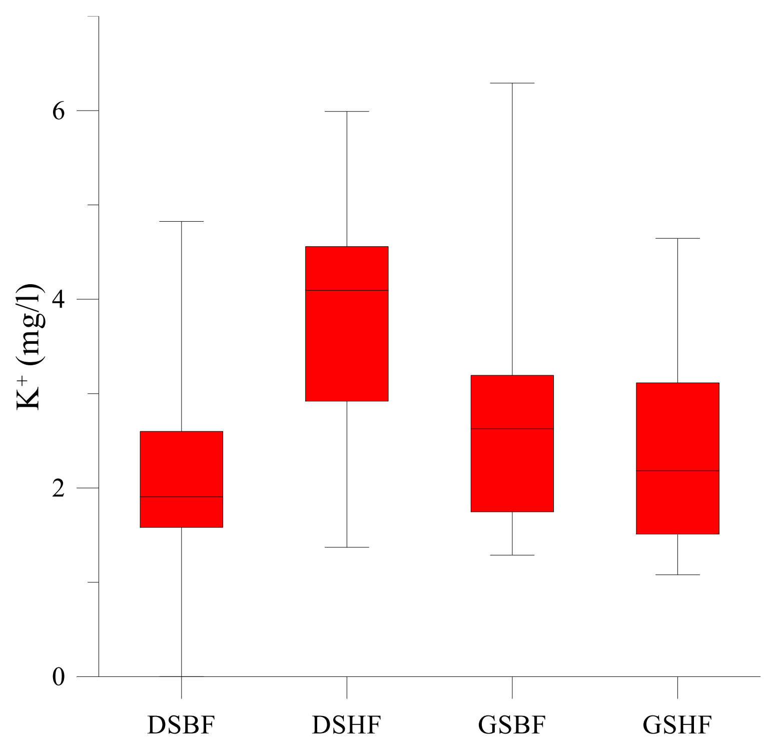
Water quality constituents	Precipitation input in GS (INPUT) (kg)	Export from Stream water in GS (OUTPUT) (kg)	Δ Storage (INPUT - OUTPUT) (kg)	% Retention
HCO_3^-	728.61	1,156.48	-427.87	-59
Na^+	521.42	544.61	-23.19	-4
Ca^{2+}	24.32	839.67	-815.35	-3353
Mg^{2+}	23.50	331.10	-307.60	-1309
K^+	355.27	169.04	186.23	52
H^+	3,266.48 *	50.05 *	3,216.43 *	98

* equivalents

The K^+ ion concentration showed distinct seasonal trend similar to other cations, with peak ion concentration observed in the transition period from the growing seasons and the subsequent dormant season (Figure 21A). There was a distinct declining trend in K^+ ion concentration from the start of the dormant season towards the end of this season and then there was a rising trend from the start of the growing season towards the end of this season. As potassium is an essential macro-nutrient for vegetative growth, there was no significant difference in the K^+ ion concentrations between the growing season base flow and high flow samples, indicating the assimilation of potassium by the vegetation during this season (Figure 21B and Table 11). The dormant season high flow concentrations were significantly higher than the dormant season base flow and growing season high flow samples (Table 11). This indicates the flushing of K^+ ions by decaying vegetation during the high flow events in the dormant season and the K^+ ions being actively cycled by vegetation during the growing season. Further, unlike the other major cations, the mean K^+ ion concentration for high flow samples was 1.37 times higher than the mean of the base flow concentrations. Thus, there is a direct relationship between discharge and K^+ ion concentrations (Likens et al., 1967). The yield (kg/ha/cm) of K^+ ion concentration was 80% less in the growing season as compared to the dormant season of the water year 2016 (Table 9). The mass balance analysis for the growing season 2016 showed 52% retention of K^+ ion as compared to atmospheric inputs (Table 10).



A.



B.

Figure 21: (A.) Scatter plot of MC5 stream's K^+ concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's K^+ concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

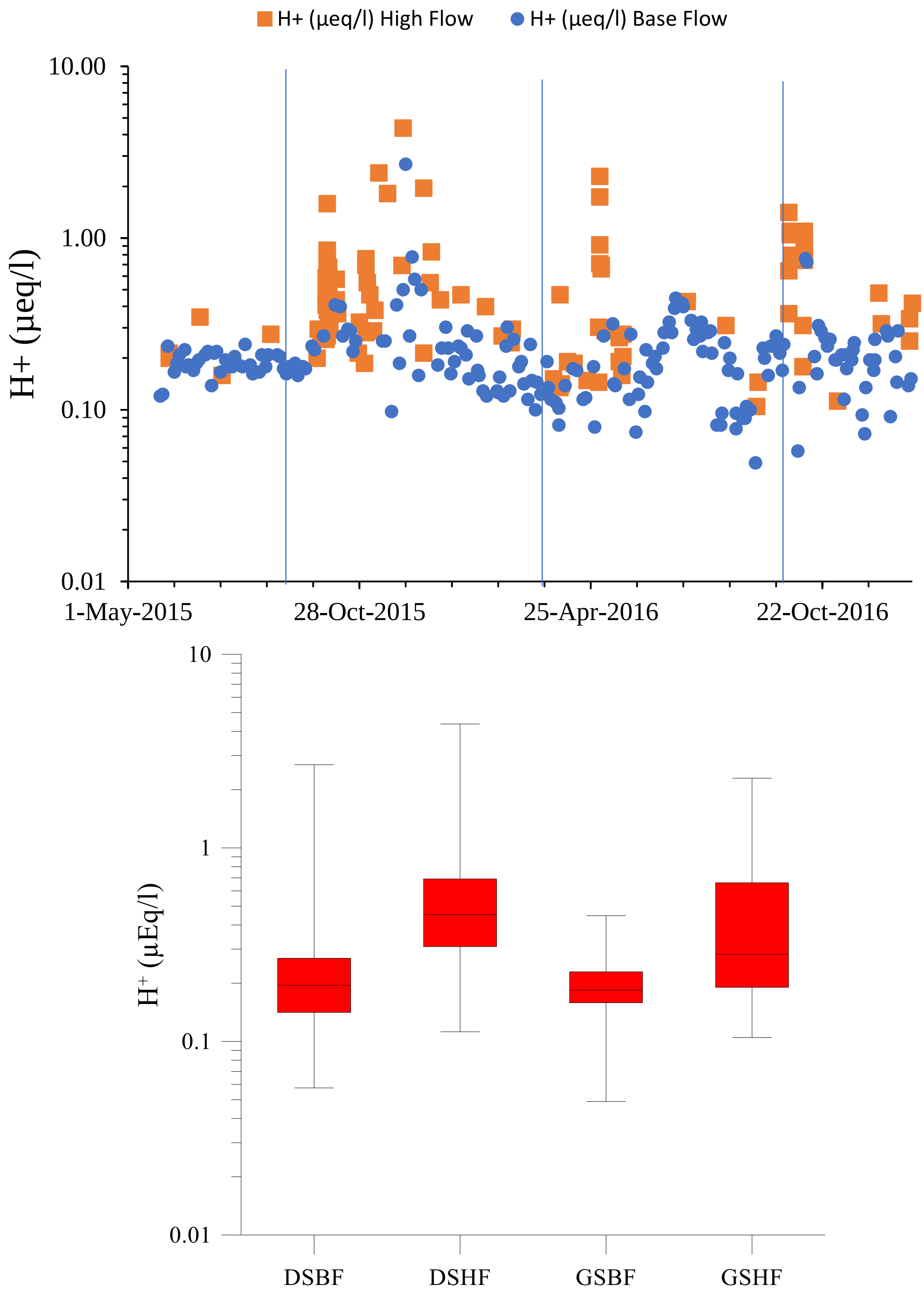
Table 11: Kruskal-Wallis post hoc test, showing pair-wise significant differences between DSBF, DSHF, GSBF and GSHF for MC5 stream's conductivity, HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, K^+ and H^+ ion concentrations from May 26, 2015 to December 31, 2016

Water quality constituents	GSBF – DSBF (Comparison 1)	GSBF – GSHF (Comparison 2)	DSBF – DSHF (Comparison 3)	GSHF – DSHF (Comparison 4)
Conductivity	0.000	0.000	0.025	1.000
HOC_3^-	0.000	0.000	.0000	0.233
Na^+	0.000	0.000	0.000	1.000
Ca^{2+}	0.000	0.000	0.015	1.000
Mg^{2+}	0.000	0.000	0.019	1.000
K^+	0.008	1.000	0.000	0.000
H^+	1.000	0.000	0.000	0.023

(Note: Shaded areas in the grid means significant differences between the groups)

H^+ showed flow specific trends, with high flow H^+ significantly higher by approximately two times than the base flow H^+ for both the seasons (Figure 22 A, B). There is no significant difference between the base flow H^+ of the dormant and the growing season, whereas the both the high flow H^+ for both of the seasons are significantly higher than the corresponding base flow H^+ ion activity (Table 11). The yield (kg/ha/cm) of H^+ ion was 70 % less during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 9). The mass balance analysis for H^+ ion for the growing season 2016 indicated a 98 % retention in the watershed (Table 10).

A.

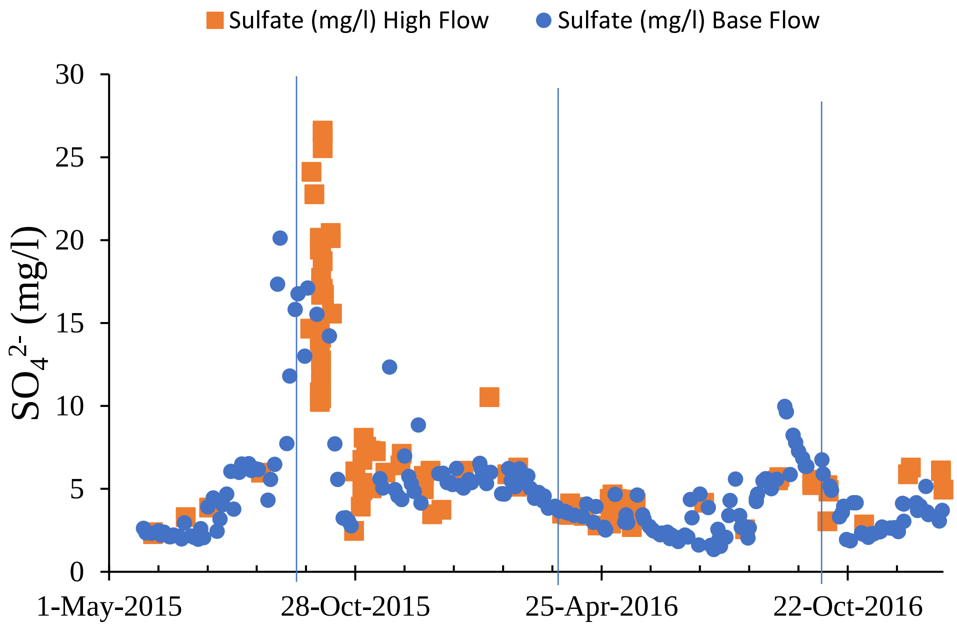


B.

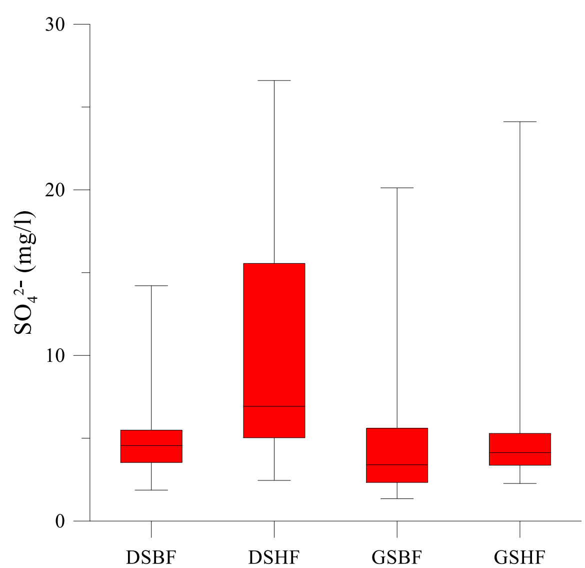
Figure 22: (A.) Scatter plot of MC5 stream's H^+ concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's H^+ concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF (Note: Y-axis of both plots are in log scale)

6.2.3 Anions (SO_4^{2-}, Cl^-, Br^-, F^-)

Both the SO_4^{2-} ion and Cl^- ion displayed similar flow specific trends for the period from May 26, 2015 to December 31, 2016, with the ionic concentrations under 10 mg/l for the whole period, except during the transition from 2015 growing season into the dormant season (Figure 23, 24). The 2015 growing season was the driest as compared to the 2016, 2017 and growing season normals by 11%, 39% and 19% respectively (Figure 3, Table 2). The months of May, June and July 2015 had significantly lower precipitation than the normals for those months. The gradual increase in HCO_3^-, Na^+, Ca^{2+} and Mg^{2+} ionic concentration in the stream water during this period suggest that the stream was recharged by the deeper groundwater. The shallow ground water wells at the study site, installed to monitor wetland parameters showed an average increase of 0.5 meter in water level during the dormant season of water year 2016 as compared to the lowest monthly elevation of ground water measured in growing seasons of water year 2015. In the months of August and September 2015, intermittent precipitation, aided the flushing of the $SO4^{2-}$ and Cl^- ions from the mineralized organic matter deposited in the upper regolith during the prolonged preceding dry period (Rice & Bricker, 1995). Thus, significantly higher concentrations of SO_4^{2-} and Cl^- ions was seen in the baseflow concentrations during these months (Figure 23A, 24A). Further, there was a significant rain event (October 2 to October 4, 2015) with cumulative precipitation of 9.11 cm. This rain event after this significant dry period lead to further flushing of mineralized organic matter and thus a distinct peak in the high flow stream water samples collected during this period as seen in Figure 23 and 24. A similar trend is seen during the end of growing season of water year 2016, but since it was not preceded by an extreme dry period and subsequent flushing rain event, a lesser distinct peak was observed. The base flow and high flow samples concentration ranges overlap as seen in the scatter plots, but statistically the dormant season high flow concentrations of both of these ions was significantly higher as compared to the dormant season base flow and growing season high flow (Table 14). The yield (kg/ha/cm) of Cl^- ion and SO_4^{2-} ion was 66% and 80% less, respectively during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 12). The mass balance analysis for Cl^- ion and SO_4^{2-} ion for the growing season 2016 indicated a 20 % and 58% retention, respectively in the watershed as compared to the atmospheric inputs (Table 13).

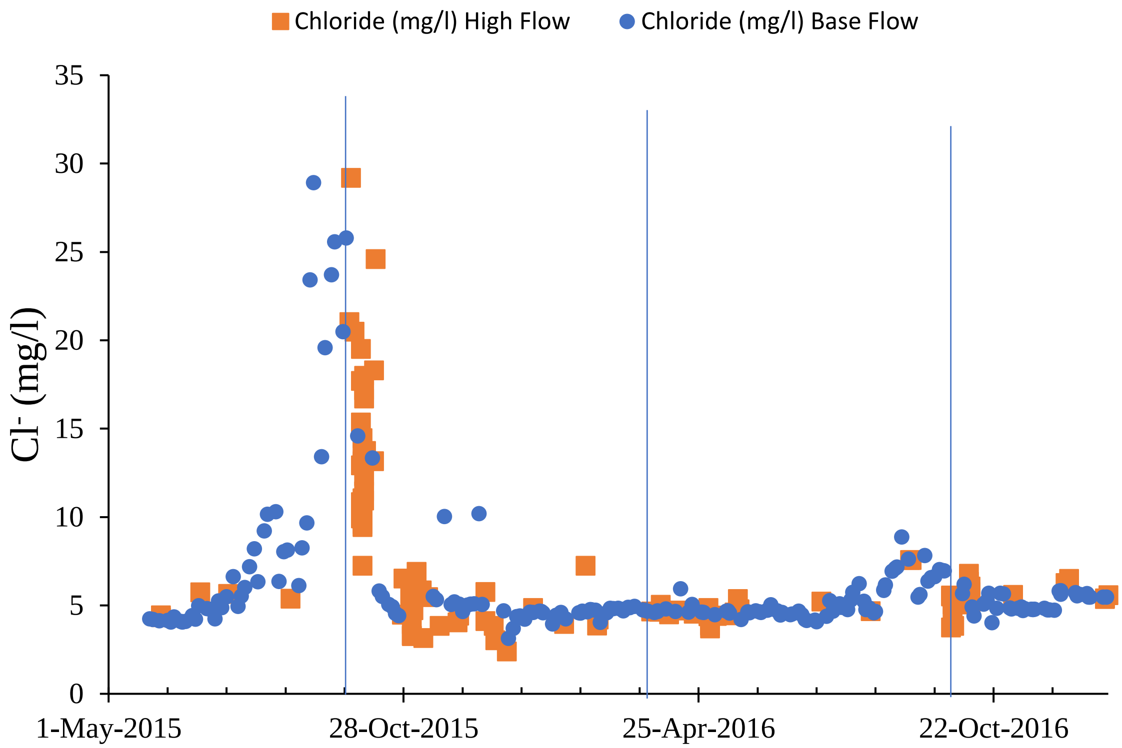


A.



B.

Figure 23: (A.) Scatter plot of MC5 stream's SO_4^{2-} concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's SO_4^{2-} concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF



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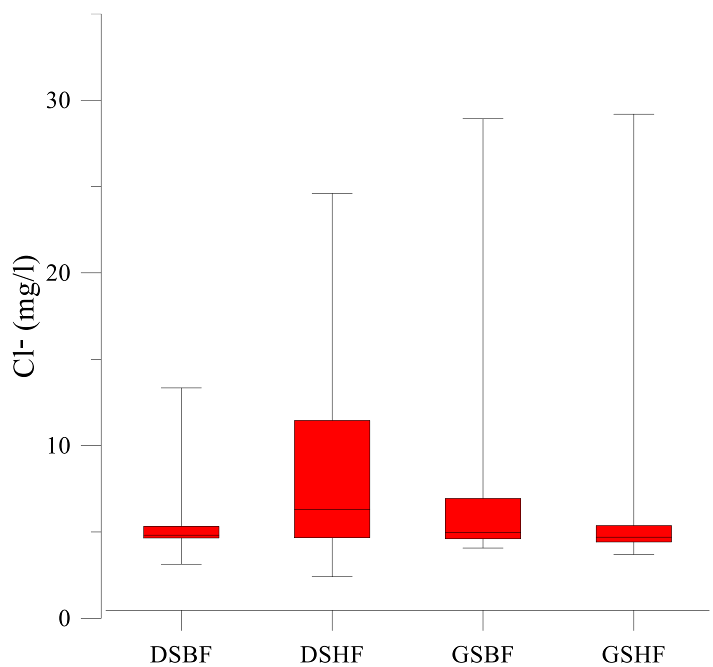


B.

Figure 24: (A.) Scatter plot of MC5 stream's Cl^- concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's Cl^- concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

Table 12: Hydrochemical transport of MC5 watershed's SO_4^{2-}, Cl^-, Br^- and F^- for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituents	Dormant season			Growing season		
	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)
SO_4^{2-}	2,489.06 ± 154.53	10.683 ± 0.663	0.1375 ± 0.0085	329.86 ± 11.32	1.416 ± 0.049	0.0278 ± 0.0010
Cl^-	1,914.74 ± 106.57	8.218 ± 0.457	0.1058 ± 0.0059	423.28 ± 11.92	1.817 ± 0.051	0.0357 ± 0.010
Br^-	6.33 ± 0.20	0.027 ± 0.001	0.0003 ± 0.0000	2.55 ± 0.05	0.011 ± 0.000	0.0002 ± 0.0000
F^-	59.62 ± 5.22	0.256 ± 0.022	0.0033 ± 0.0003	13.16 ± 0.88	0.056 ± 0.003	0.0011 ± 0.0001

Table 13: Mass balance of MC5 watershed's SO_4^{2-}, Cl^-, Br^- and F^- from the for the growing season of water year 2016 (April 1, 2016 to September 31, 2016)

Water quality constituents	Precipitation input in GS (INPUT) (kg)	Export from Stream water in GS (OUTPUT) (kg)	Δ Storage (INPUT - OUTPUT) (kg)	% Retention
SO_4^{2-}	782.78	329.86	452.92	58
Cl^-	530.26	423.28	106.98	20
Br^{-*}	0.00	2.55	-2.55	100
F^-	256.73	13.16	243.57	95

Table 14: Kruskal-Wallis post hoc test, showing pair-wise significant differences between DSBF, DSHF, GSBF and GSHF for MC5 stream's SO_4^{2-}, Cl^-, Br^- and F^- ion concentrations from May 26, 2015 to December 31, 2016

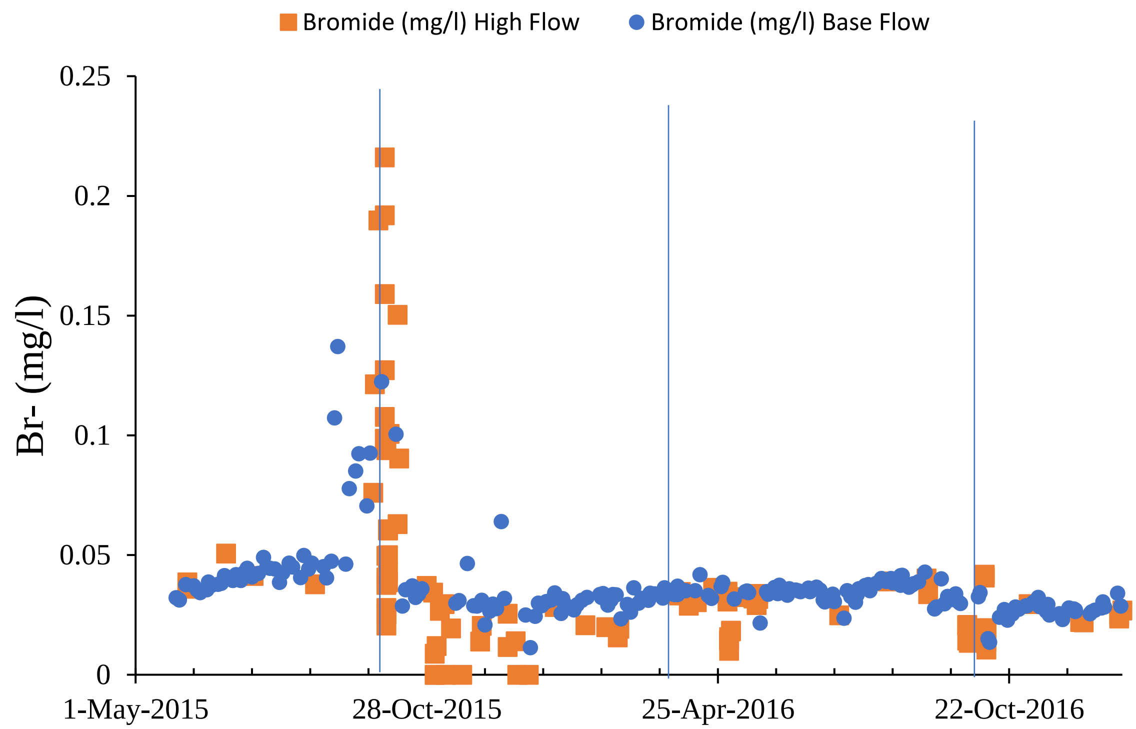
Water quality constituents	GSBF – DSBF (Comparison 1)	GSBF – GSHF (Comparison 2)	DSBF – DSHF (Comparison 3)	GSHF – DSHF (Comparison 4)
SO_4^{2-}	0.304	1.000	0.000	0.000
Cl^-	0.297	0.189	0.001	0.001
Br^-	0.000	0.000	1.000	1.000
F^-	0.000	0.156	0.000	1.000

(Note: Shaded areas in the grid means significant differences between the groups)

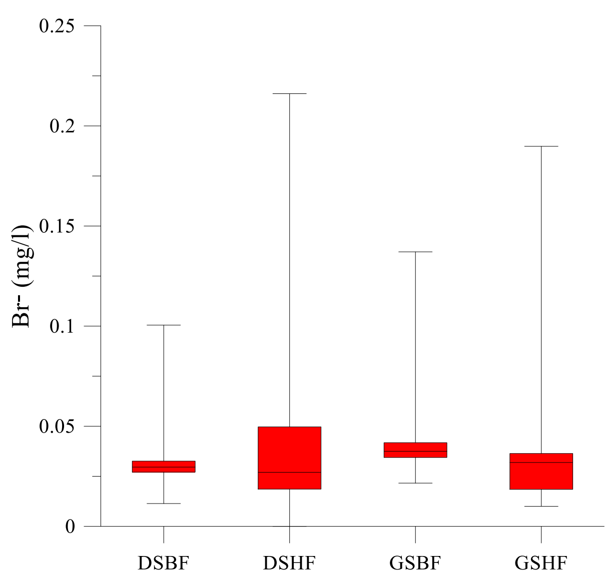
The Br^- ion concentrations for all the period from May 26, 2016 to December 31, 2016, remained under the 0.05 mg/l, except during the end of the growing season 2015 and the subsequent rain event in the dormant season (October 2 to October 4, 2015) (Figure 25 A). Also, the Br^- ionic concentrations shows a seasonal trend with a slight increase towards the end of the growing seasons as seen in the trend in both the growing seasons of water year 2015 and 2016. As discussed in the section of SO_4^{2-} and Cl^- ionic concentration, the growing season 2015 was the driest season, followed immediately by a large rain event. The peaks in the base flow and high flow stream water samples as seen in the scatter plot of Br^- concentration is explained by the bromination of the soil organic matter (Leri & Ravel, 2015). The shedding of the foliage during the end of the growing season and the intermittent rainfall in the months of August and September 2015, aided in the complex abiotic and microbially mediated reaction of halogenation. Thus, a distinct peak in Br^- ion concentration is seen in the base flow samples during the end of growing season 2015 and then the subsequent flushing of Br^- ions by the high flow event lead to a 4 times higher concentration (0.21 mg/l) as compared to the base level concentration (0.05 mg/l) measured for the majority of the analytical period.

The statistical analysis showed growing season base flow Br^- concentrations were significantly higher as compared to the dormant season base flow and growing season high flow water samples (Table 14). There was no significant difference in the high flow samples of both the seasons and between the two flow types in the dormant season. The yield (kg/ha/cm) of Br^- ions was 33% less during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 12). Br^- ion was not detected in the precipitation samples of the growing season 2016.

Bromide concentrations in surface water is United States are typically low, with average values inland ranging from 0.014 to 0.2 mg/l. The MC5 stream Br^- concentrations for the study period were below 0.05 mg/l except during the October 2015 rain event and the preceding dry period. The discharge of bromide is largely unregulated in United States because of its high human toxicity threshold. However, the formation of disinfection by-products (DBPs) during drinking water treatment is of high concern. Adverse human health outcomes of DBPs have been documented and so bromide concentrations in surface waters which are sources for drinking water are of high concern (Vanbriesen, 2013). Concentrations of bromide in rain, in the form of bromide ion are typically below 0.01 mg/l (Flury & Papritz, 1993). No bromide was detected in the bulk precipitation of the growing season 2016. Anthropogenic sources of bromide include pesticides and fertilizers.



A.



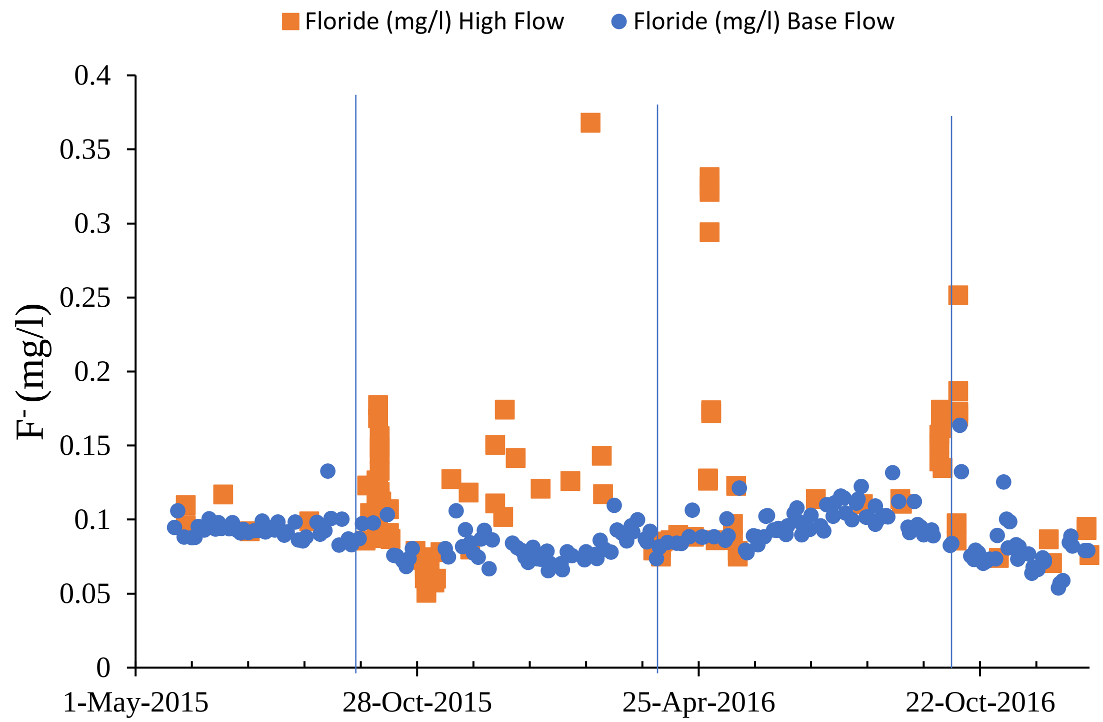
B.

Figure 25: (A.) Scatter plot of MC5 stream's Br^- concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's Br^- concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

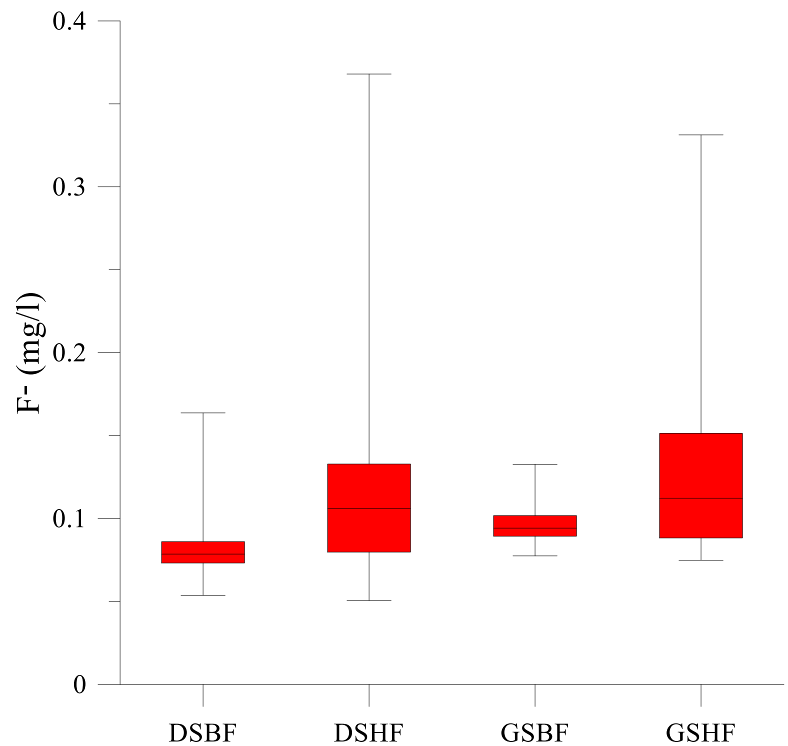
Stream water F^- ion concentrations displayed flow specific trends, with approximately 1.2 times higher concentrations during the high flow as compared to the base flow stream water samples (Figure 26 A). The concentration of F^- ion was significantly higher during the high flow of the dormant season compared to the base flow of the dormant season (Table 14). Further, it was significantly higher in the base flow of the growing season compared to the base flow of the dormant season. There was no significant difference in F^- ion concentration between the high flows of the dormant and growing season of water year 2016 (Table 14).

Fluoride is naturally found in rocks and is found in groundwater because of leaching from rock formations. At the same time, fluoride has anthropogenic sources including manufacturing activities in smelters, fertilizer factories and ceramic and glass manufacturing. Fluoride has important biological effects, especially for vegetation, and in soils contaminated with fluoride, the content of organic matter declines as does the activity of microorganisms (Walna et al., 2013).

With the present data, it is difficult to ascertain the source of fluoride in the high flow of the dormant season, but the shallow hydrologic flowpaths and lesser residence time leading to influence of precipitation chemistry on the stream water could be one of the reasons (Rice & Bricker, 1995). The yield (kg/ha/cm) of F^- ions was 67 % less during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 12). The mass balance analysis for F^- ions for the growing season 2016 indicated a 95 % retention in the watershed as compared to the atmospheric inputs as measured by bulk precipitation (Table 13).



A.



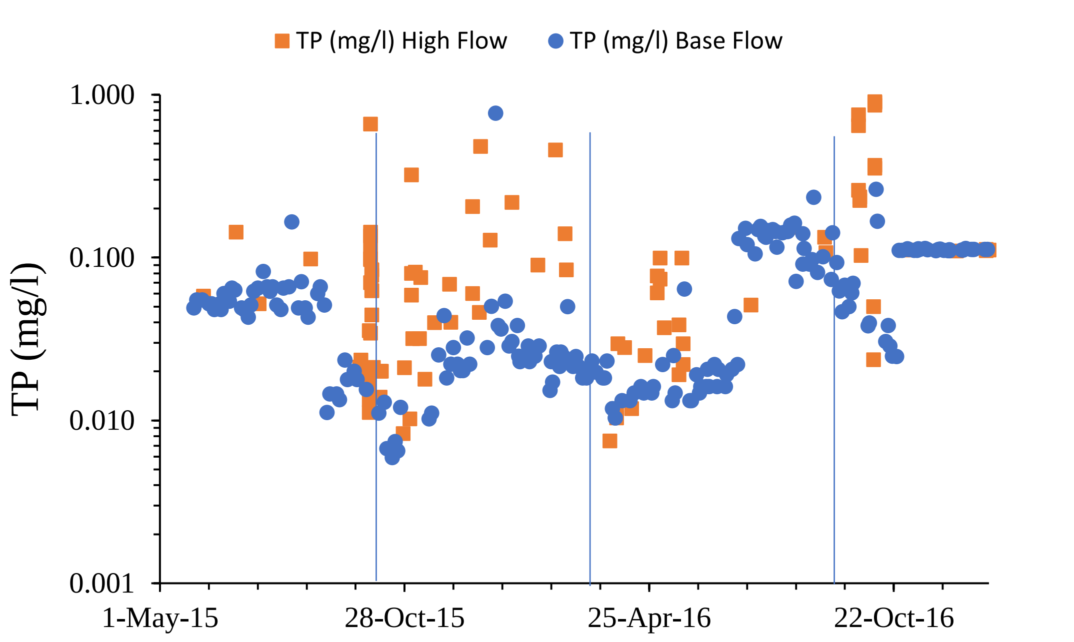
B.

Figure 26: (A.) Scatter plot of MC5 stream's F^- concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's F^- concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

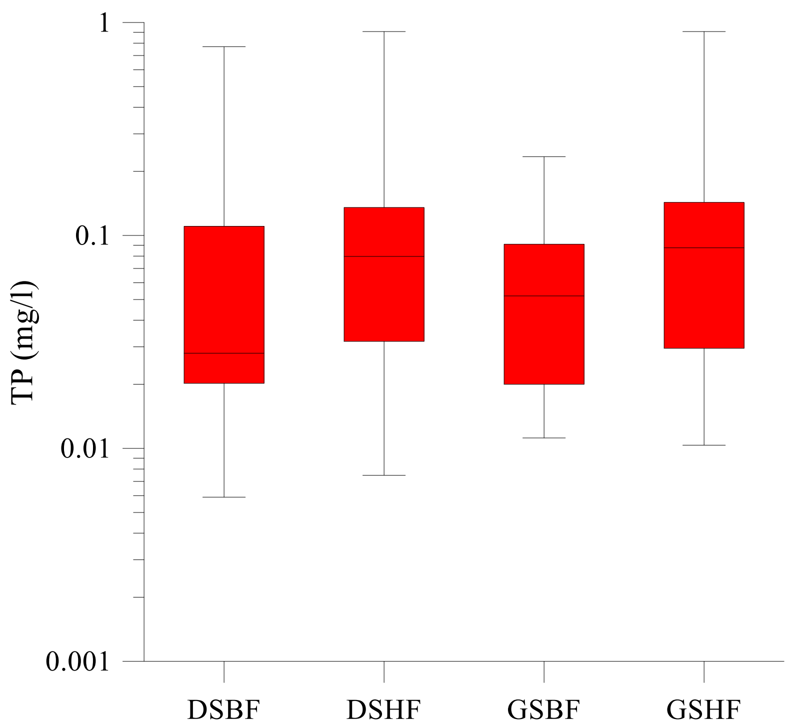
6.2.4 Phosphorous

Stream water TP during the study period (May 26, 2015 to December 31, 2016) showed a distinct flow specific trend with high flow concentrations (mean of 0.132 mg/l) significantly higher than the base flow concentration (mean of 0.062 mg/l) (Figure 27). The high flow of the dormant season showed significantly higher concentrations than the base flow of the dormant season (Table 17). It also showed a seasonality trend with base flow concentrations declining during the transition between both the growing and dormant seasons. Phosphorous is a limiting nutrient for algal growth in freshwater ecosystems, with a TP value of 0.037 mg/l being the reference concentration for the S.E. Ecoregions IX (Allan et al., 2013). The yield (kg/ha/cm) for TP was 3.7 times higher in the growing season as compared to the dormant season for the water year 2016 (Table 15). The mass balance analysis for TP for the growing season of water year 2016 showed 42% retention in the watershed as compared to the atmospheric inputs (Table 16).

The TDP concentrations showed a seasonal trend and a flow specific trend prior to the initiation of construction activity in the watershed with base flow concentrations for the most part below 0.04 mg/l (Figure 28A). From the period from March 2016 to December 2016 the TDP concentrations began to display a distinct variability and a twofold increase. As per watershed survey, the land clearing started in March 2016 in the eastern region of the watershed, which potentially increased the erosion and led to the increase in the flux of TDP in the stream. From this region the first order stream (Tributary East) of the watershed originate, with drainage area of approximately 14% of the MC5 watershed. The seasonal and flow specific groupings did not show any statistical difference (p=.095) (Table 17). The yield (kg/ha/cm) of TDP was 75% less during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 15). The mass balance analysis for TDP for the growing season of water year 2016 showed 92% retention in the watershed as compared to the atmospheric inputs (Table 16). For the study period, the TDP concentration was approximately 70% of the TP concentration.

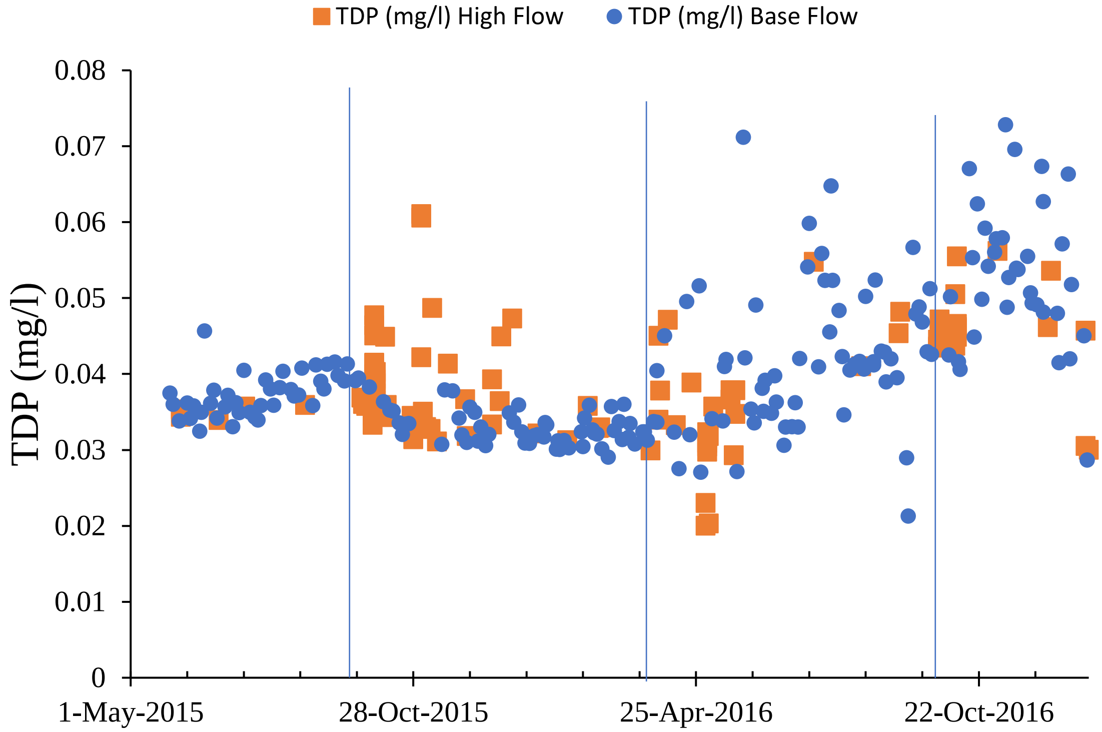


A.



B.

Figure 27: (A.) Scatter plot of MC5 stream's TP concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's TP concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF (Note: Y-axis of both plots are in log scale)



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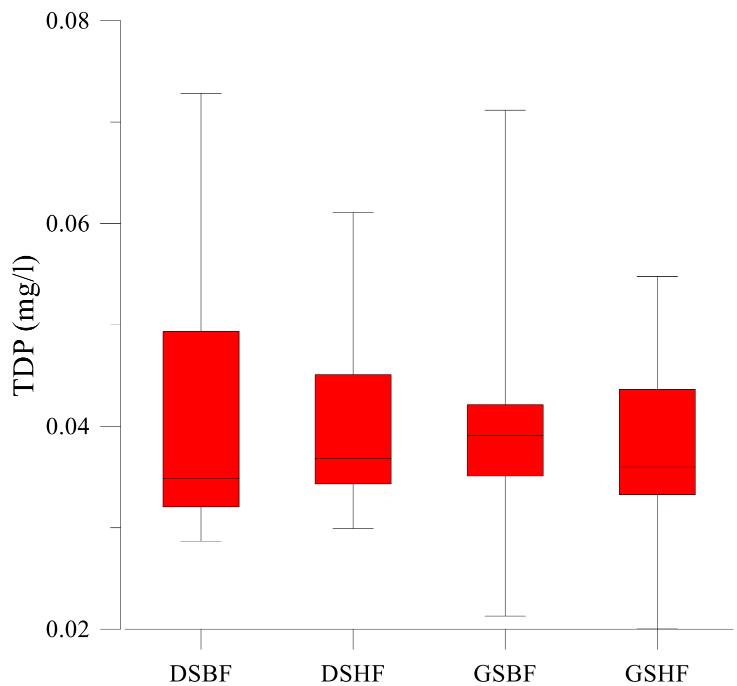


B.

Figure 28: (A.) Scatter plot of MC5 stream's TDP concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's TDP concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

Table 15: Hydrochemical transport of MC5 watershed's TP, TDP, PO_4^{3-}, DOP, and PP for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituents	Dormant season			Growing season		
	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / hectare / cm)	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)
TP	62.24 ± 5.72	0.267 ± 0.025	0.0034 ± 0.0003	149.38 ± 18.19	0.641 ± 0.078	0.0126 ± 0.0015
TDP	21.09 ± 1.69	0.091 ± 0.007	0.0012 ± 0.0001	3.50 ± 0.10	0.015 ± 0.000	0.0003 ± 0.0000
PO_4^{3-}	22.72 ± 2.45	0.098 ± .010	0.0013 ± 0.0001	0.12 ± 0.01	0.001 ± 0.000	0.0000 ± 0.0000
DOP	0.00 ± 0.00	0.000 ± 0.000	0.0000 ± 0.0002	3.38 ± 0.01	0.014 ± 0.007	0.0003 ± 0.0015
PP	41.15 ± 4.31	0.176 ± 0.019	0.0022 ± 0.0002	145.88 ± 18.10	0.626 ± 0.078	0.0123 ± 0.0015

Table 16: Mass balance of MC5 watershed's TDP and PO_4^{3-} for the growing season of water year 2016 (April 1, 2016 to September 31, 2016)

Water quality constituents	Precipitation input in GS (INPUT) (kg)	Export from Stream water in GS (OUTPUT) (kg)	Δ Storage (INPUT - OUTPUT) (kg)	% Retention
TP	255.78	149.38	106.40	42
TDP	45.02	3.50	41.52	92
PP	210.76	145.88	64.88	31
PO_4^{3-}	180.09	0.12	179.97	~100

Table 17: Kruskal-Wallis post hoc test, showing pair-wise significant differences between DSBF, DSHF, GSBF and GSHF for MC5 stream's TP, TDP, PO_4^{3-}, DOP, and PP concentrations from May 26, 2015 to December 31, 2016

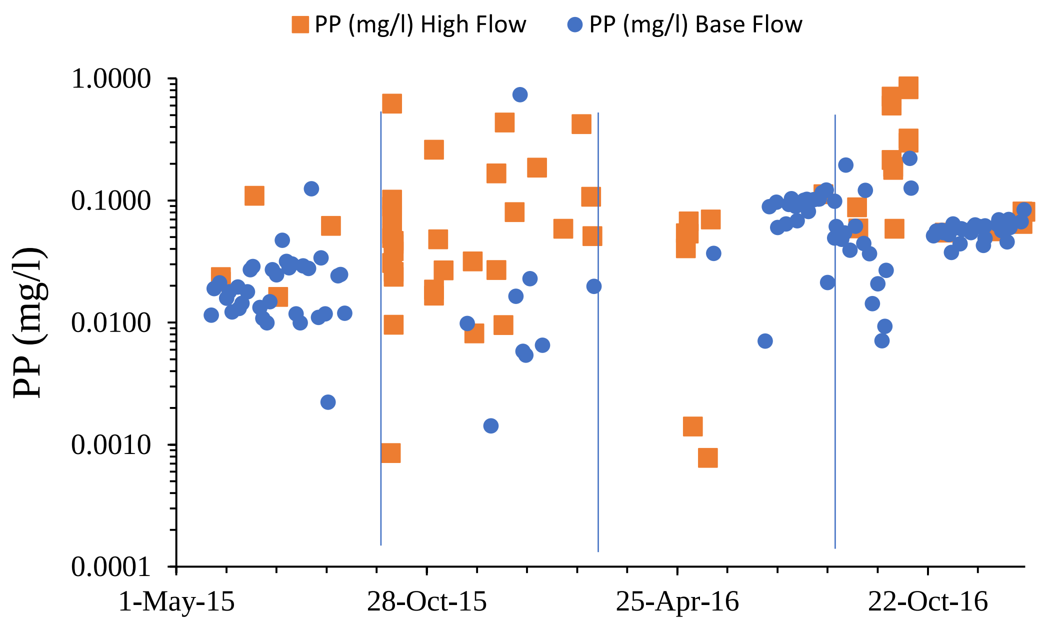
Water quality constituents	GSBF – DSBF (Comparison 1)	GSBF – GSHF (Comparison 2)	DSBF – DSHF (Comparison 3)	GSHF – DSHF (Comparison 4)
TP	0.765	0.971	0.010	1.000
TDP	0.095			
PO_4^{3-}	0.113			
DOP	1.000	1.000	0.000	0.048
PP	0.068	1.000	0.002	1.000

The PP concentrations showed flow specific trend with high flow concentrations (mean of 0.09 mg/l) significantly higher than the baseflow concentrations (0.03 mg/l) (Figure 29). The yield (kg/ha/cm) was 6 times higher in the growing season as compared to the dormant season for the water year 2016 (Table 15). For the study period, the PP concentration was approximately 30% of the TP concentration.

The PO_4^{3-} ion concentration was predominantly detected in the high flow samples of the MC5 stream water (Figure 30 A, B). Only during the end of the 2015 growing season did the base flow samples show concentrations rising from approximately 0.02 to 0.07 mg/l, similar to the trend seen in the SO_4^{2-} and Cl^- baseflow concentration. This is attributed to the prolonged dry period during the growing season 2015 followed by intermittent rain events, aiding in the flushing of mineralized organic matter. The PO_4^{3-} ion concentration show a normal distribution (p=.279) (Table 5) and hence the one-way analysis of variance was performed and it did not show any significant differences between the DSBF, DSHF, GSBF and GSHF groups (Table 17). The yield of PO_4^{3-} was 0.001 kg/ha/cm for the dormant season 2016 (Table 15). The mass balance analysis for PO_4^{3-} for the growing season of water year 2016 showed approximately 100% retention in the watershed as compared to the atmospheric inputs (Table 16). The PO_4^{3-} concentration was approximately 15 percent of TDP concentration for the study period.

The DOP concentrations was approximately 85% of TDP concentration and it showed a similar trend to that of TDP. After mid- March 2016 the concentrations of DOP showed high variability and a twofold increase above the base levels of 0.04 mg/l observed during pre-construction sampling period (Figure 31). There is a faint seasonality in the DOP concentrations, with declining trend during the transition period from growing to the dormant season. The DOP concentration was significantly less in the dormant season high flow as compared to the dormant season base flow and growing season high flow (Table 17). The yield of DOP was 0.0003 kg/ha/cm for the growing season 2016 (Table 15).

A.



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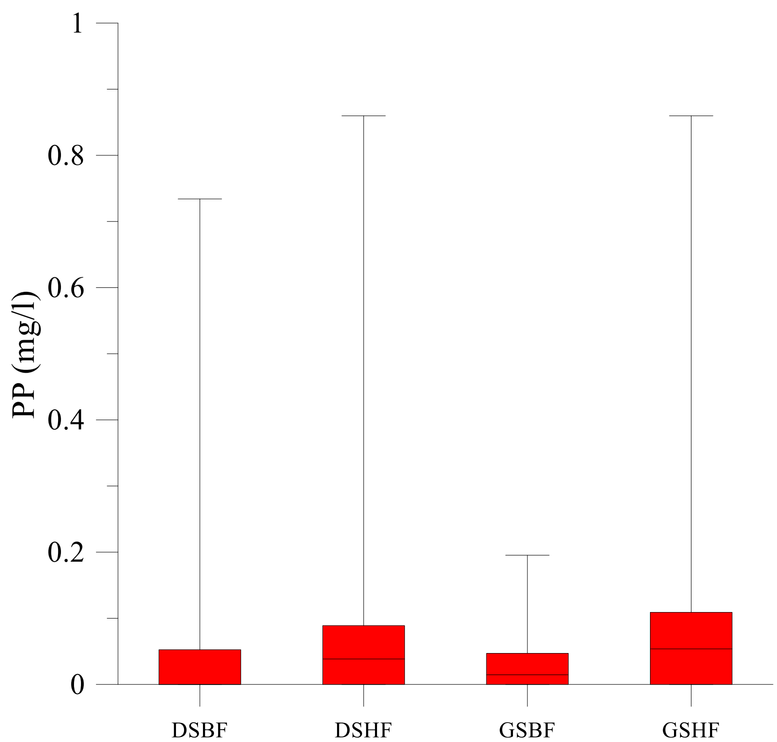
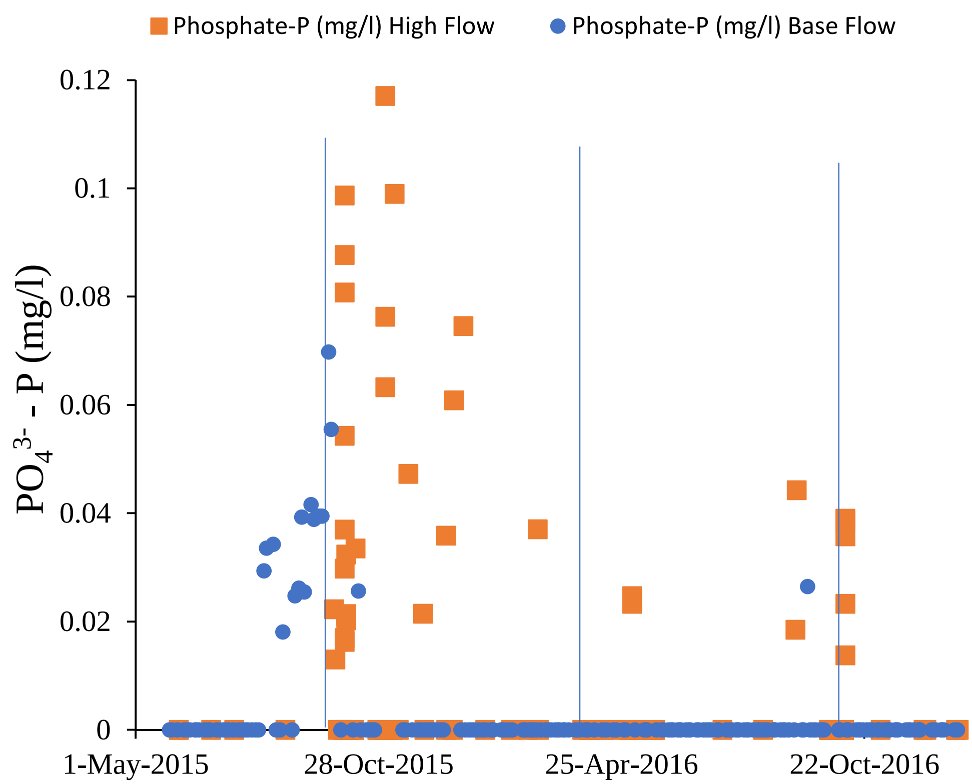


Figure 29: (A.) Scatter plot of MC5 stream's PP concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's PP concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF



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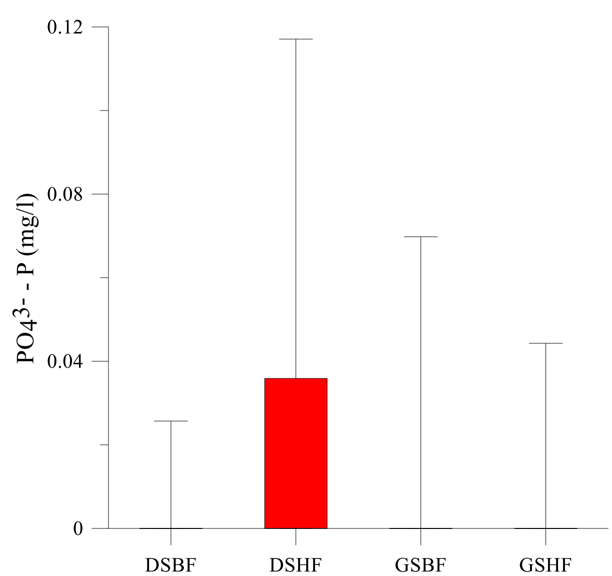
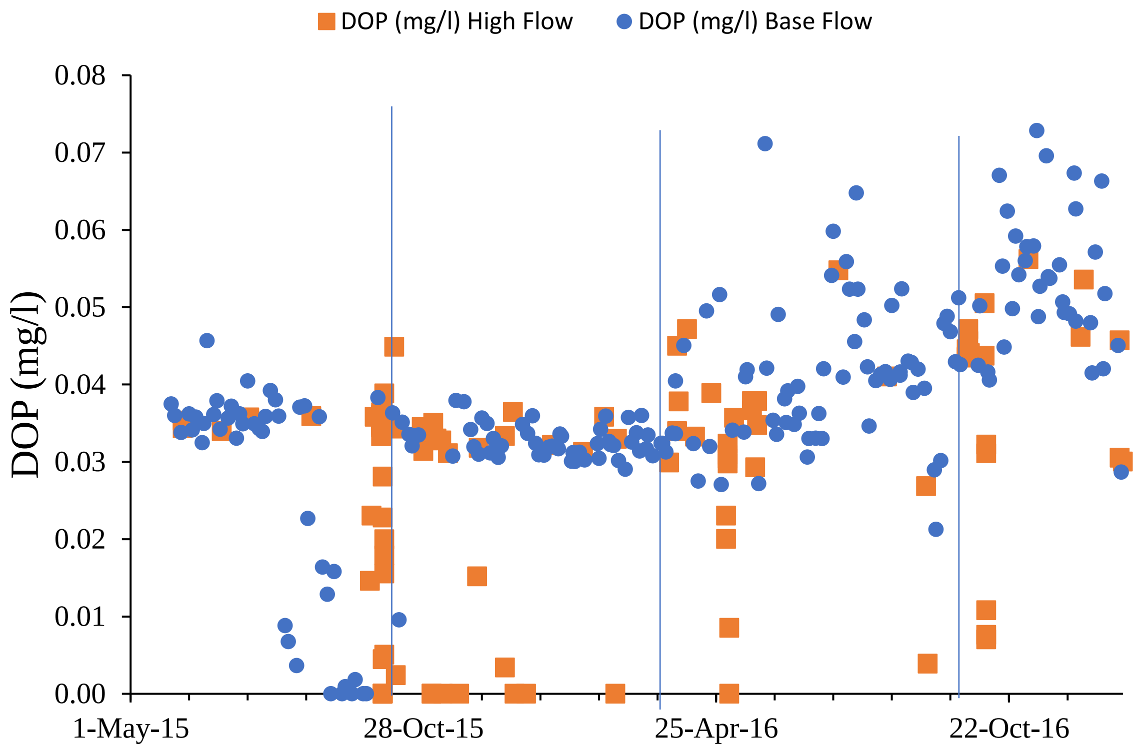
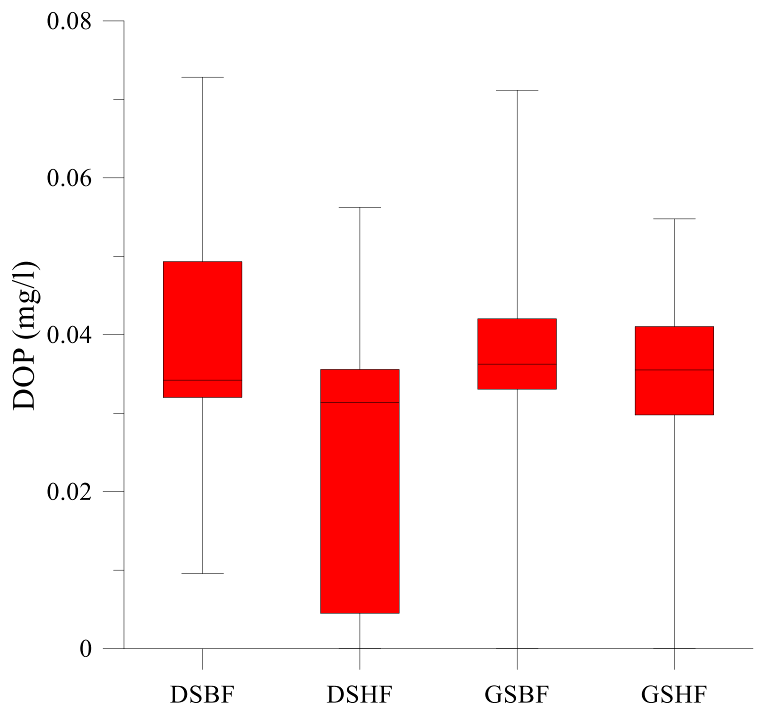


B.

Figure 30: (A.) Scatter plot of MC5 stream's PO_4^{3-} concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's PO_4^{3-} concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF



A.



B.

Figure 31: (A.) Scatter plot of MC5 stream's DOP concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's DOP concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

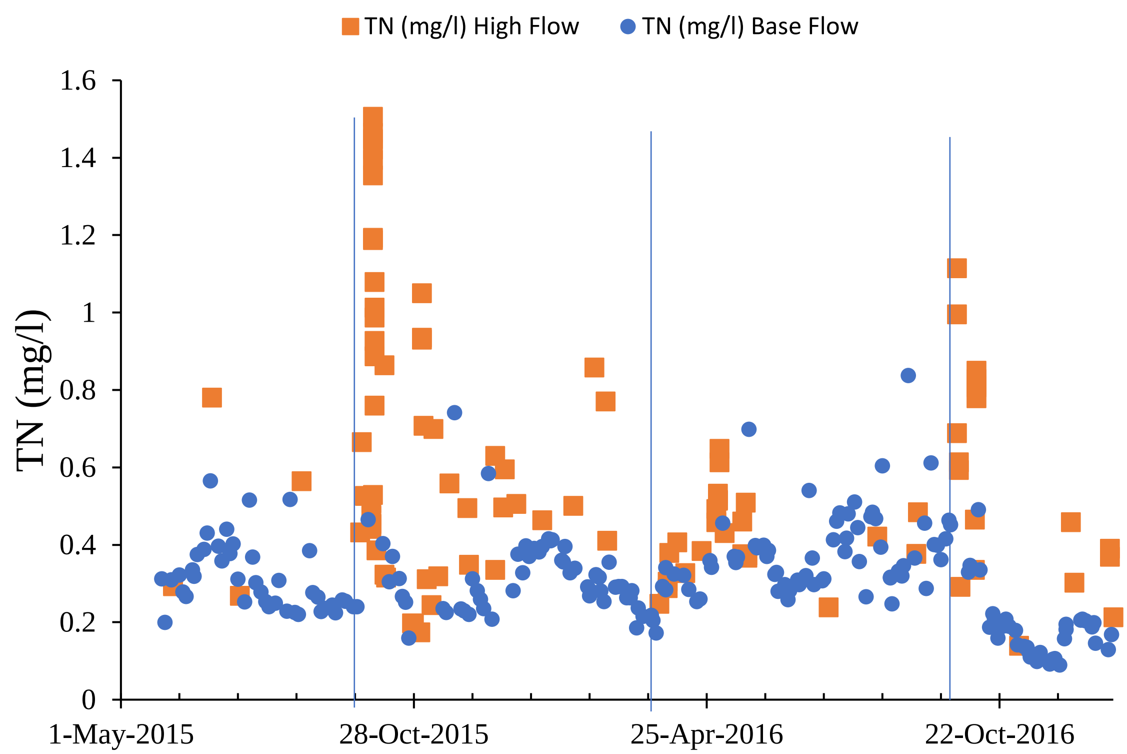
6.2.5 Nitrogen

Stream water TN concentrations display flow specific trends, with high flow concentrations significantly higher than the base flow concentrations across the analytical period (Figure 32). The mean TN baseflow concentration was 0.31 mg/l and the mean TN high flow concentration was 0.60 mg/l. The reference concentration for TN for the S.E. Ecoregion IX is 0.692 mg/l (Allan et al., 2013). The TDN constituted approximately 95% of TN and mirror the flow specific trend, with dormant season high flow concentrations approximately two times that of base flow and growing season high flow concentrations (Figure 33). Statistically, there was no significant difference between the high flow samples of dormant and the growing season (Table 20). The yield (kg/ha/cm) of TN and TDN was an average 76% less, during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 18). The mass balance analysis for TN and TDN for the growing season 2016 indicates an average 92% retention, in the watershed as compared to the atmospheric inputs (Table 19).

The PN concentrations showed a similar pattern as observed for the TDP and DOP concentrations. The PN concentration prior to the beginning of construction activity on the watershed was primarily negligible, except during the high rain event in October 2015 and constitutes approximately 1% of the TN (Figure 34). From March 2016, which was when the land clearing activity on the eastern side of the watershed began, the PN concentration showed an increasing trend and variability. In the growing season of water year 2016, the PN concentrations rose 3 times and constitutes approximately 9% of the TN. As the dormant season of water year 2017 began, it had gradually declined, indicating the land stabilization could be the reason of the declining trend in the PN concentration. For the study period, the PN concentration was approximately 5% of the TN concentration. Also, because of the variability in the PN concentrations pre and during construction activity, the statistical analysis showed significant difference in the base flow and the high flow of both the dormant and the growing seasons (Table

20).

A.



B.

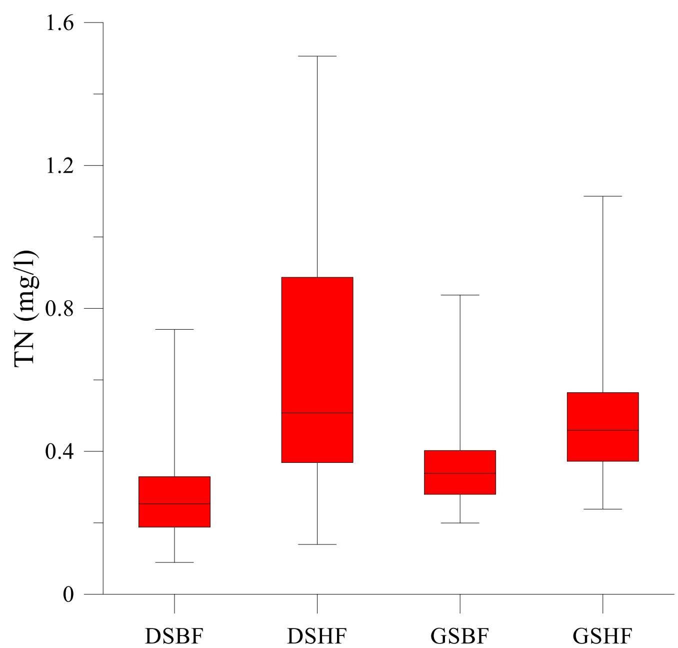
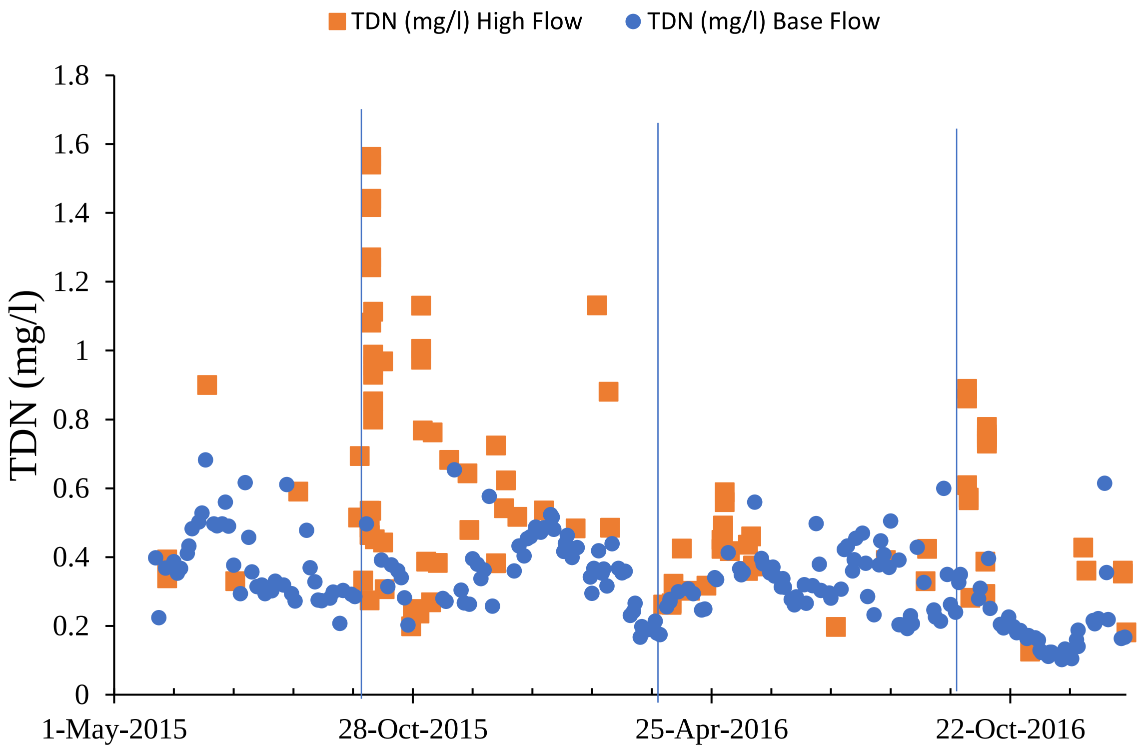


Figure 32: (A.) Scatter plot of MC5 stream's TN concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's TN concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

A.



B.

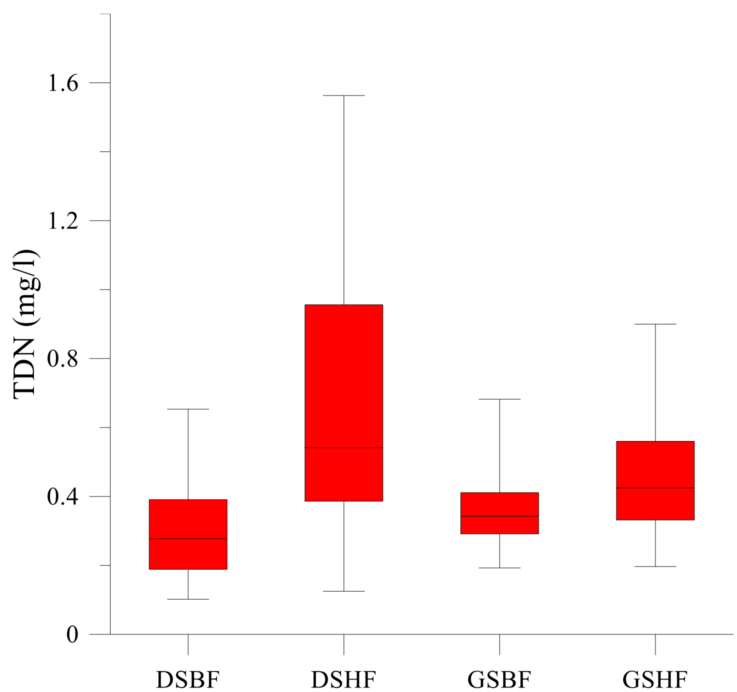
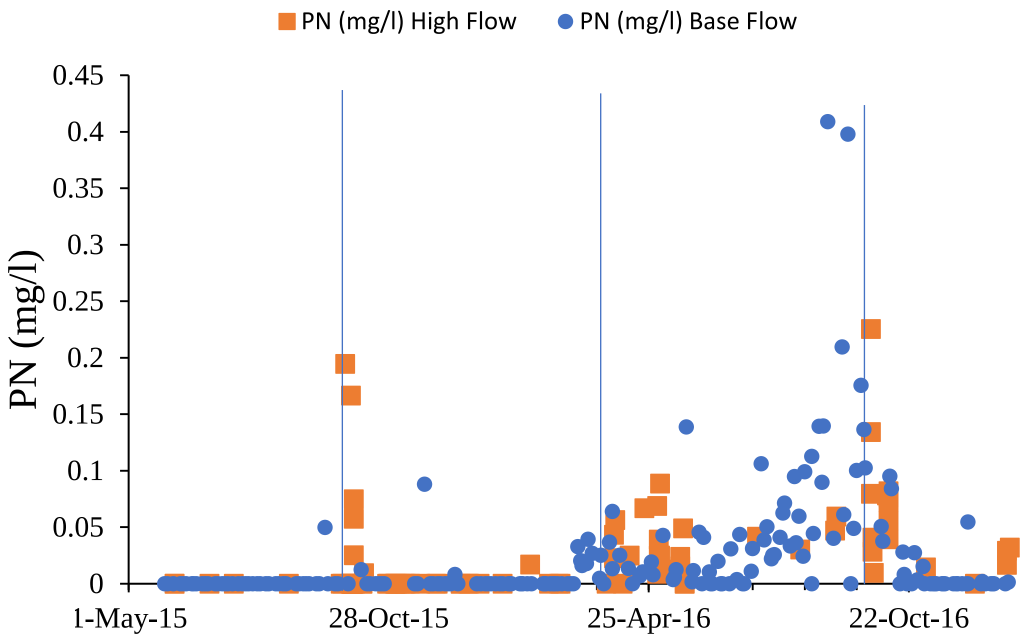


Figure 33: (A.) Scatter plot of MC5 stream's TDN concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's TDN concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

A.


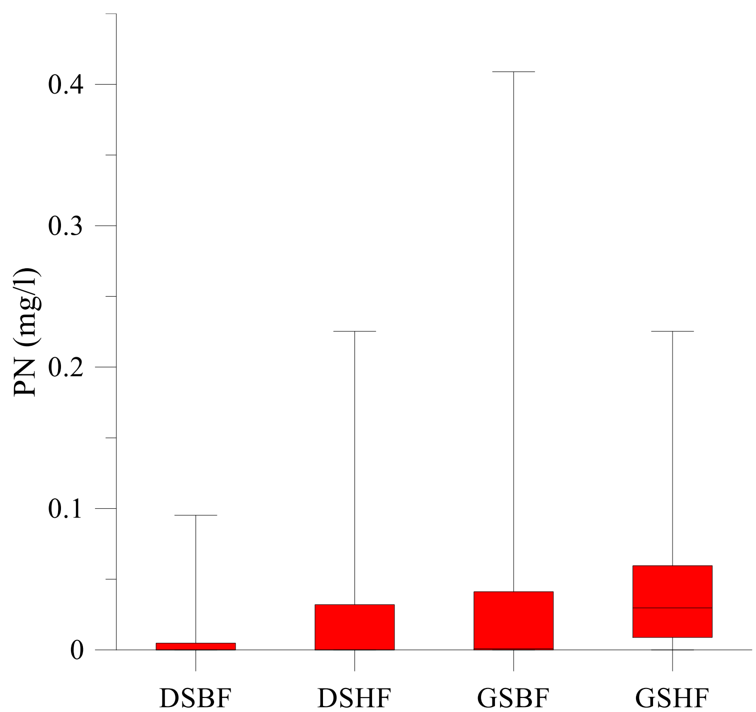
B.


Figure 34: (A.) Scatter plot of MC5 stream's PN concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's PN concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

Table 18: Hydrochemical transport of MC5 watershed's TN, TDN, PN, NO_3^-, NH_4^+ and DON for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituent	Dormant season			Growing season		
	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)
TN	247.58 ± 19.63	1.063 ± 0.084	0.0137 ± 0.0010	39.92 ± 1.64	0.171 ± 0.007	0.0034 ± 0.0001
TDN	246.09 ± 20.54	1.057 ± 0.088	0.0136 ± 0.0011	36.52 ± 1.47	0.157 ± 0.006	0.0031 ± 0.0001
PN	1.49 ± 0.17	0.006 ± 0.001	0.0001 ± 0.0000	3.40 ± 0.19	0.014 ± 0.001	0.0003 ± 0.0000
NO_3^-	145.38 ± 10.50	0.624 ± 0.045	0.0080 ± 0.0005	20.31 ± 0.98	0.087 ± 0.004	0.0017 ± 0.0000
NH_4^+	37.65 ± 2.57	0.162 ± 0.011	0.0021 ± 0.0001	11.29 ± 0.25	0.048 ± 0.001	0.0010 ± 0.0000
DON	63.06 ± 7.75	0.271 ± 0.033	0.0035 ± 0.0004	4.92 ± 0.33	0.022 ± 0.011	0.0004 ± 0.0000

Table 19: Mass balance of MC5 watershed's TN, TDN, PN, NO_3^- and NH_4^+ for the growing season of water year 2016 (April 1, 2016 to September 31, 2016)

Water quality constituents	Precipitation input in GS (INPUT) (kg)	Export from Stream water in GS (OUTPUT) (kg)	Δ Storage (INPUT - OUTPUT) (kg)	% Retention
TN	566.53	39.92	526.60	93
TDN	407.07	36.52	370.55	91
PN	159.46	3.40	156.06	98
NO_3^-	261.13	20.31	240.82	92
NH_4^+	309.59	11.29	298.29	96

Table 20: Kruskal-Wallis post hoc test, showing pair-wise significant differences between DSBF, DSHF, GSBF and GSHF for MC5 stream's TN, TDN, PN, NO_3^-, NH_4^+ and DON concentrations from May 26, 2015 to December 31, 2016

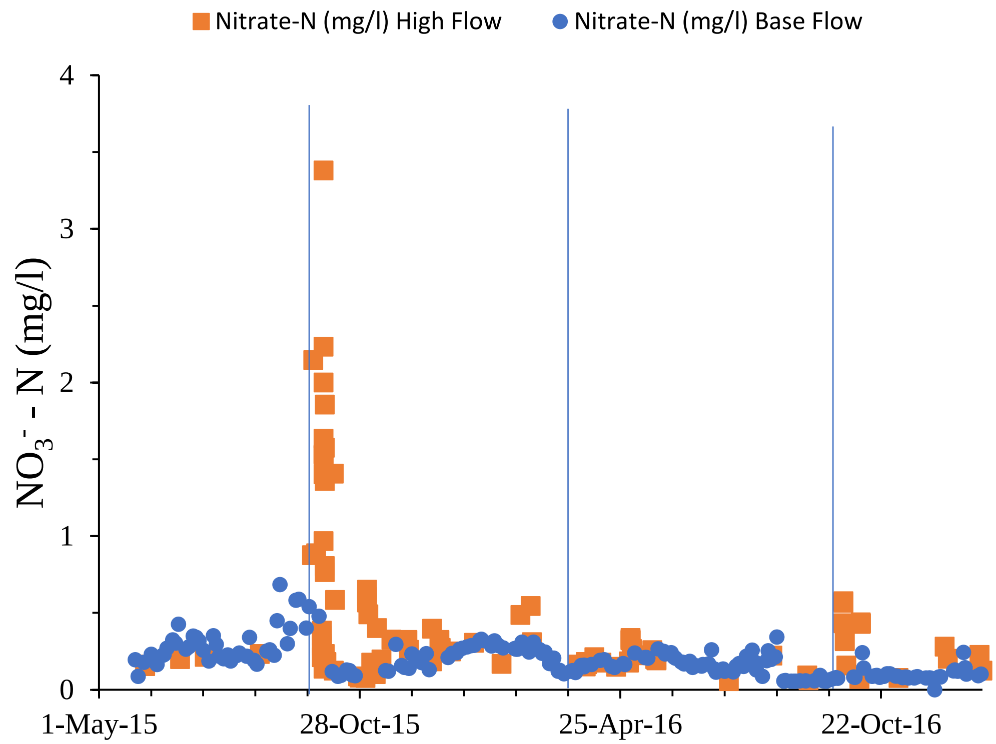
Water quality constituents	GSBF – DSBF (Comparison 1)	GSBF – GSHF (Comparison 2)	DSBF – DSHF (Comparison 3)	GSHF – DSHF (Comparison 4)
TN	0.000	0.004	0.000	1.000
TDN	0.011	0.023	0.000	0.325
PN	0.002	0.078	1.000	0.000
NO_3^-	0.207	0.352	0.000	0.233
NH_4^+	0.014	1.000	0.365	0.747
DON	1.000	1.000	0.027	1.000

(Note: Shaded areas in the grid means significant differences between the groups)

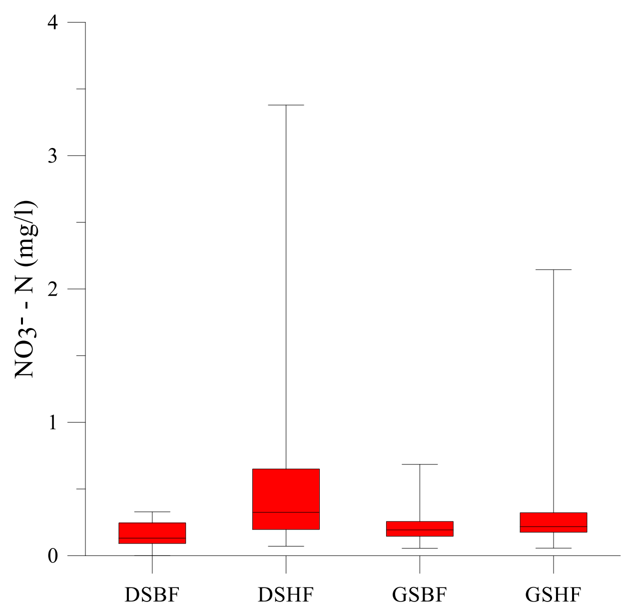
Stream water NO_3^--N concentration show a flow specific trend, similar to that observed in the other anions and the dormant season high flow concentration was significantly higher than the dormant season base flow concentrations (Figure 35, Table 20). The NO_3^--N ion concentration constituted approximately 63% of the TDN concentration and for the most part of the study period was under 1 mg/l, except during the October 2015 rain event. As per the NC surface water quality criterion for water supply watershed, the NO_3^--N benchmark is 10 mg/l (Allan et al., 2013). The yield (kg/ha/cm) of NO_3^- -N was 78% less, during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 17). The mass balance analysis for NO_3^- -N for the growing season 2016 indicates an average 92% retention, in the watershed as compared to the atmospheric inputs (Table 18).

Stream water NH_4^+ concentrations constituted approximately 27 % of the TDN concentrations and the mean NH_4^+ concentration for the analytical period was 0.107 mg/l (Figure 36). There was no significant difference between the flow types and only the base flow of the growing season was significantly higher in NH_4^+ concentration as compared to the dormant season base flow concentration (Table 20), which indicates ammonification of organic matter during the growing season (Ladd & Jackson, 1982). The yield (kg/ha/cm) of NH_4^+ was 52% less, during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 17). The mass balance analysis for NH_4^+ for the growing season 2016 indicates an average 96% retention, in the watershed as compared to the atmospheric inputs (Table 18).

Stream water DON concentrations constituted approximately 10% of the TDN concentrations and displayed a flow specific trend with dormant season high flow concentrations significantly higher than the base flow concentrations (Figure 37). The mean of the dormant and growing season's high flow concentrations was 0.112 mg/l and that of dormant and growing season's base flow concentration was 0.053 mg/l. The yield (kg/ha/cm) of DON was 88% less, during the growing season as compared to the dormant season of water year 2016 for the MC5 watershed (Table 17).



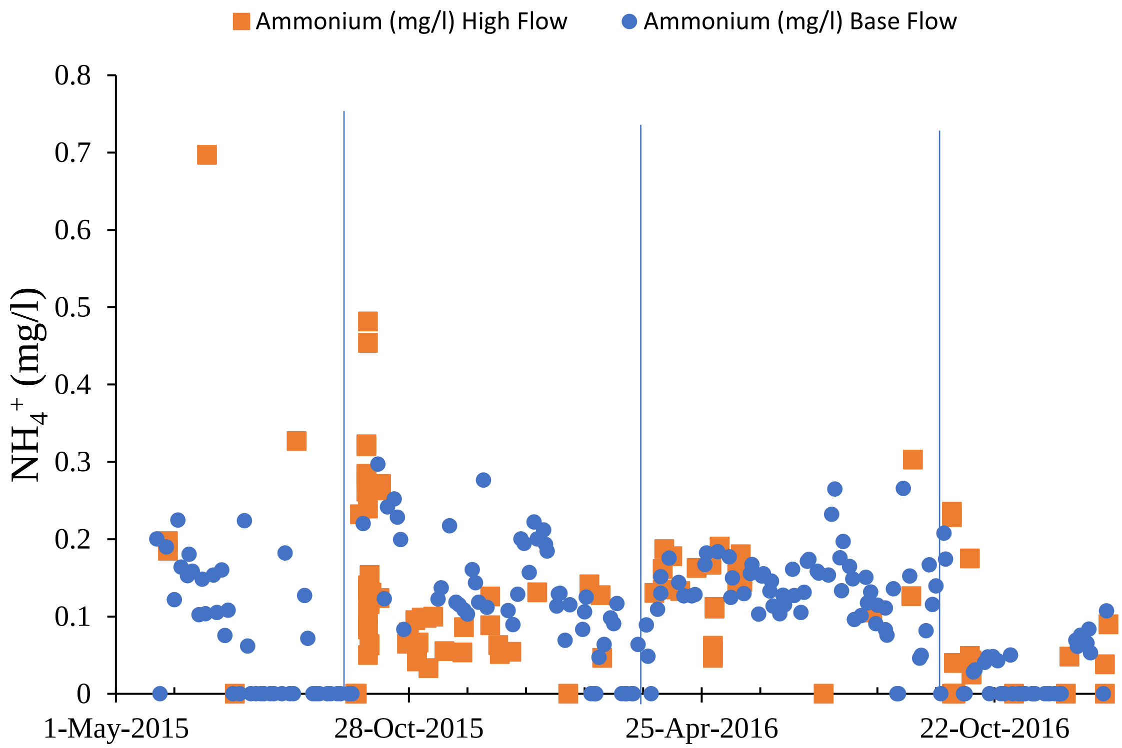
A.



B.

Figure 35: (A.) Scatter plot of MC5 stream's NO_3^- concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's NO_3^- concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

A.



B.

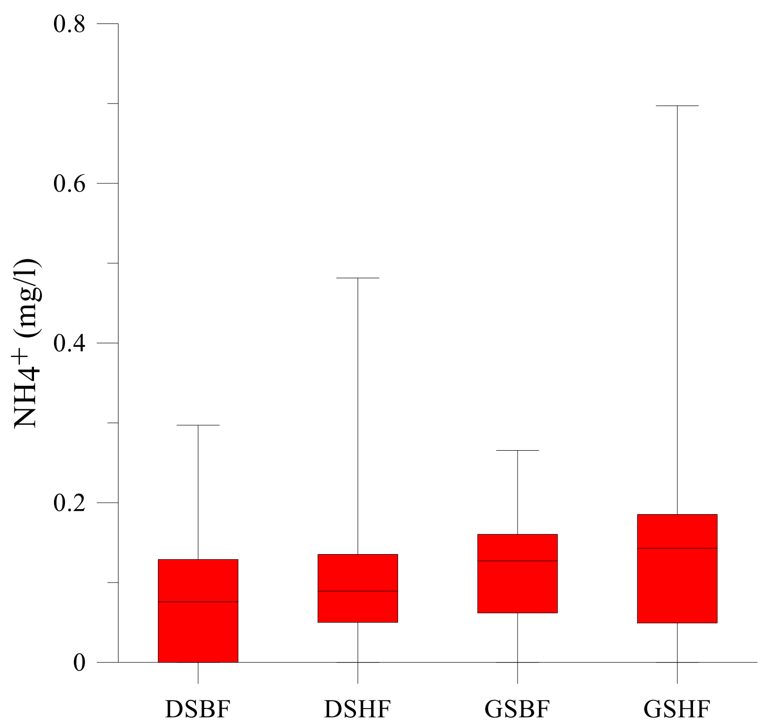
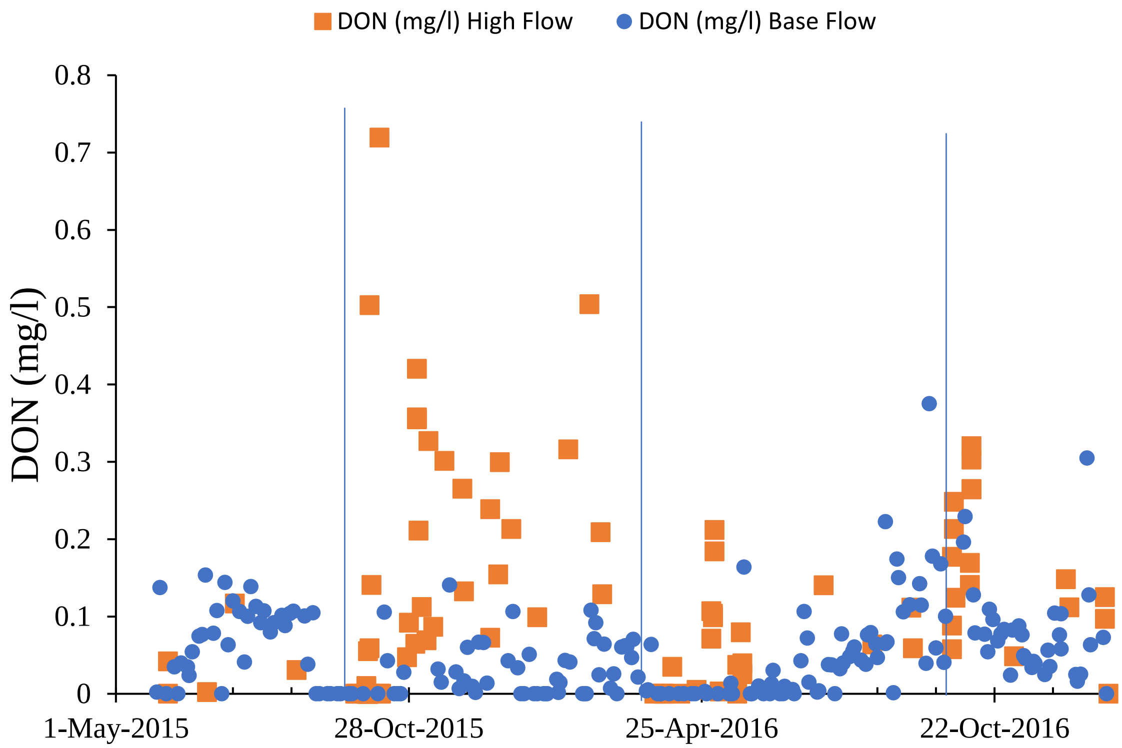


Figure 36: (A.) Scatter plot of MC5 stream's NH_4^+ concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's NH_4^+ concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

A.



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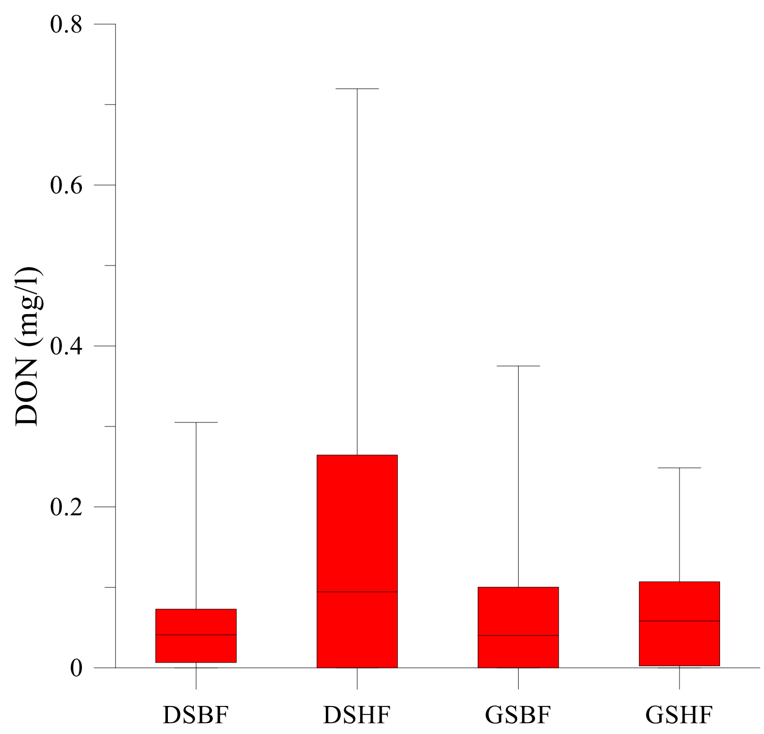


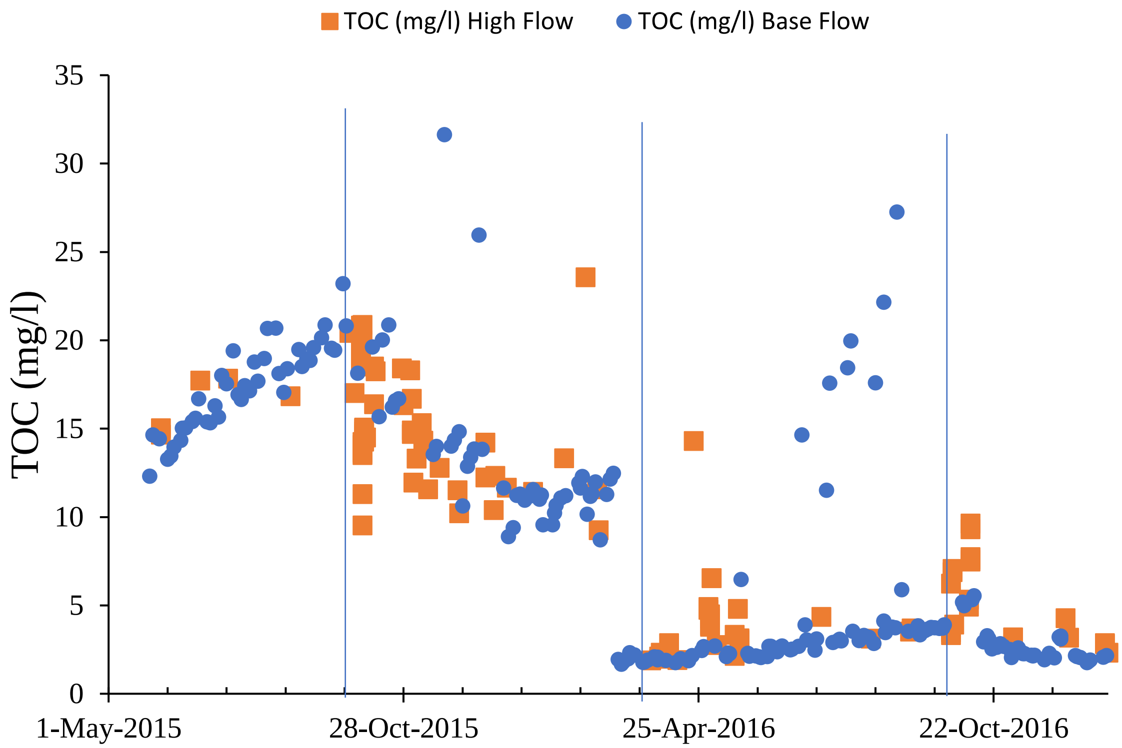
Figure 37: (A.) Scatter plot of MC5 stream's DON concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's DON concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

6.2.6 Carbon

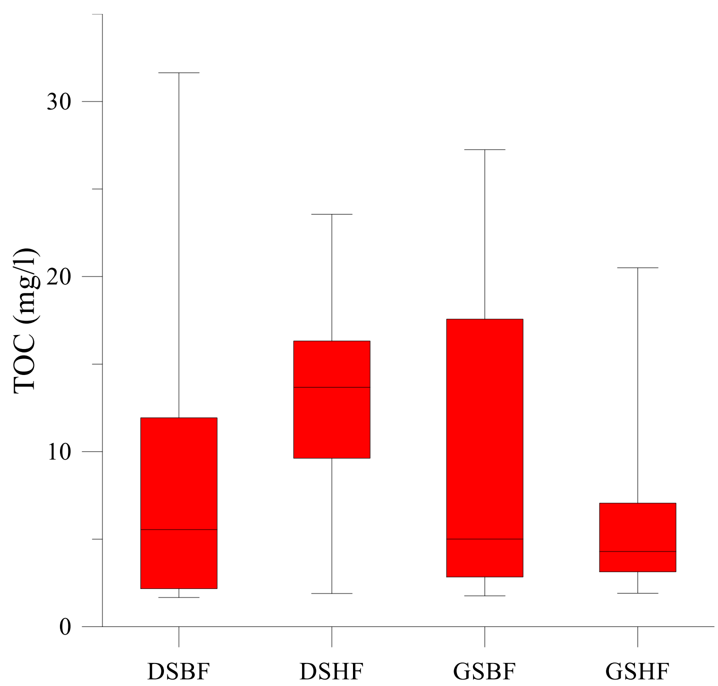
Stream water TOC concentration initially showed a distinct seasonal trend with gradual increasing trend from the growing season to dormant season and a decreasing trend from the dormant season to the growing season (Figure 38). This trend is supported by the supply of organic plant material to the stream water during the growing season followed by the fall period. The TOC concentrations ranged from approximately 10 mg/l to 20 mg/l during the growing season of 2015 and the dormant season of 2016, respectively. However, there was a sudden decline in the TOC concentrations from March 2016 and the TOC concentrations mostly remained under 5 mg/l with few exceptions (Figure 38A). This decline was in line with the time period of the initiation of the land clearing activity during March 2016 in the eastern region of the watershed. The land clearing activity likely drastically altered the hydrologic flowpaths in the Tributary East and, thus the result was reduction in TOC concentration by approximately two times. Further, the high flow TOC concentration was generally less as compared to the base flow concentrations prior to the initiation of the land clearing activity, but after March 2016 this trend was reversed (Figure 38A). This trend in flow concentration indicate the change in the supply and transport mechanism of plant derived material in the stream. The yield (kg/ha/cm) of TOC was higher by 90% in the dormant season 2016 as compared to the growing season of water year 2016 (Table 22). The mass balance analysis indicated an 82% retention of TOC during the growing season 2016 as compared to the atmospheric inputs (Table 23).

Table 21: Kruskal-Wallis post hoc test, showing pair-wise significant differences between DSBF, DSHF, GSBF and GSHF for MC5 stream’s TOC, DOC and POC concentrations from May 26, 2015 to December 31, 2016

Water quality constituents	GSBF – DSBF (Comparison 1)	GSBF – GSHF (Comparison 2)	DSBF – DSHF (Comparison 3)	GSHF – DSHF (Comparison 4)
TOC	0.007	0.710	0.000	0.004
DOC	0.017	0.006	0.000	0.009
POC	0.079	0.035	0.012	0.006



A.



B.

Figure 38: (A.) Scatter plot of MC5 stream's TOC concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's TOC concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

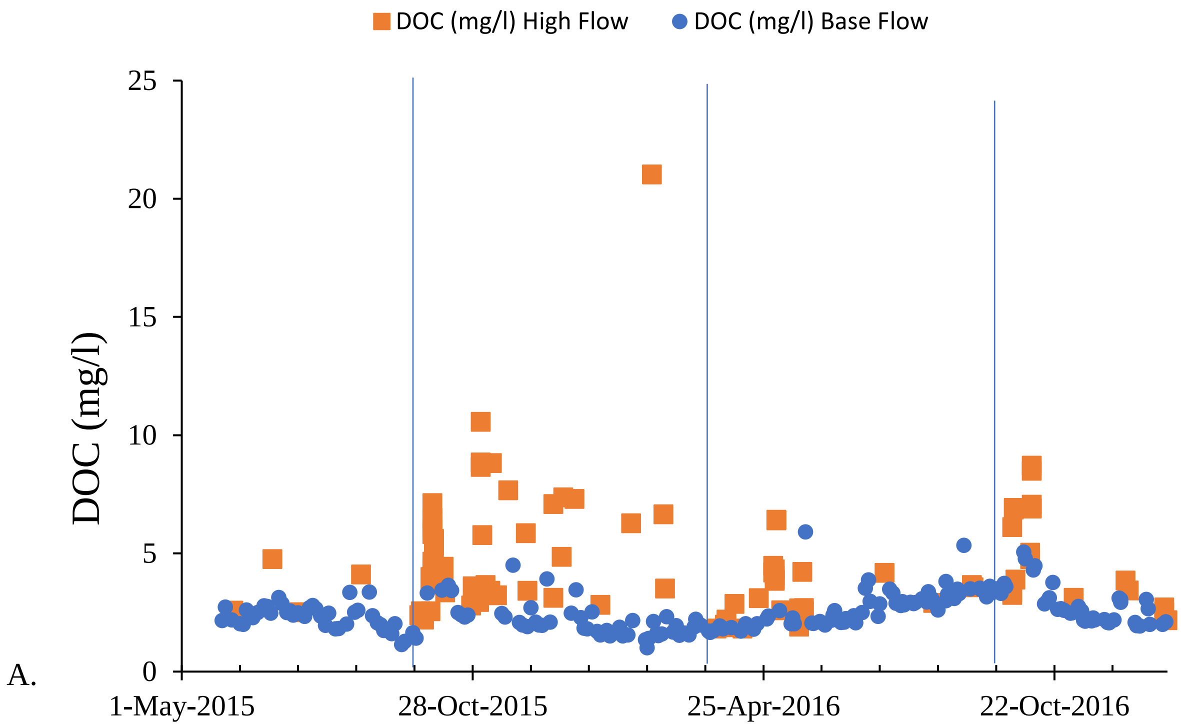
The DOC concentrations showed a flow dependent trend, with high flow concentrations (mean of 4.72 mg/l) consistently higher than the base flow concentrations (mean of 2.49 mg/l). The DOC concentrations showed consistency unlike the TOC concentration and ranged from 2 mg/l to 10 mg/l across the time period of analysis (Figure 39). The DOC concentration was approximately 23% of TOC concentration before the land clearing activity, but after that it was approximately 90% of TOC concentration. Toxic trace metals and hydrophobic pesticides bind to DOC and so DOC concentrations greater than 5 mg/l complicate water treatment and results into formation of disinfection by-products (Allan et al., 2013). There was a significant difference in the DOC concentration among all the four seasonal flow groupings (Table 21), with highest concentrations in the dormant season high flow period. The hydrochemical yield (kg/ha/cm) for DOC was higher by 84% in the dormant season 2016 as compared to the growing season of water year 2016 (Table 22). The mass balance analysis indicated an 84% retention of DOC during the growing season 2016 as compared to the atmospheric inputs (Table 23).

Table 22: Hydrochemical transport of MC5 watershed's TOC, DOC and POC for dormant season (October 1, 2015 to March 31, 2016) and growing season (April 1, 2016 to September 30, 2016) (± 1 SD estimated hydrologic and analytical uncertainties)

Water quality constituents	Dormant season			Growing season		
	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)	Export (kg)	Yield per unit area (kg / ha)	Yield per unit area per unit precipitation (kg / ha / cm)
TOC	5,952.15 ± 445.58	25.546 ± 1.912	0.3288 ± 0.0246	388.36 ± 14.78	1.667 ± 0.063	0.0328 ± 0.0012
DOC	2,898.07 ± 261.87	12.438 ± 1.124	0.1601 ± 0.0144	303.03 ± 12.26	1.301 ± 0.053	0.0256 ± 0.0010
POC	3,054.08 ± 193.46	13.108 ± 0.830	0.1687 ± 0.0106	85.33 ± 6.16	0.366 ± 0.026	0.0072 ± 0.0005

Table 23: Mass balance of MC5 watershed's TOC, DOC and POC for the growing season of water year 2016 (April 1, 2016 to September 31, 2016)

Water quality constituents	Precipitation input in GS (INPUT) (kg)	Export from Stream water in GS (OUTPUT) (kg)	Δ Storage (INPUT - OUTPUT) (kg)	% Retention
TOC	2,116.19	388.36	1,727.83	82
DOC	1947.59	303.03	1,644.56	84
POC	168.61	85.33	83.28	49



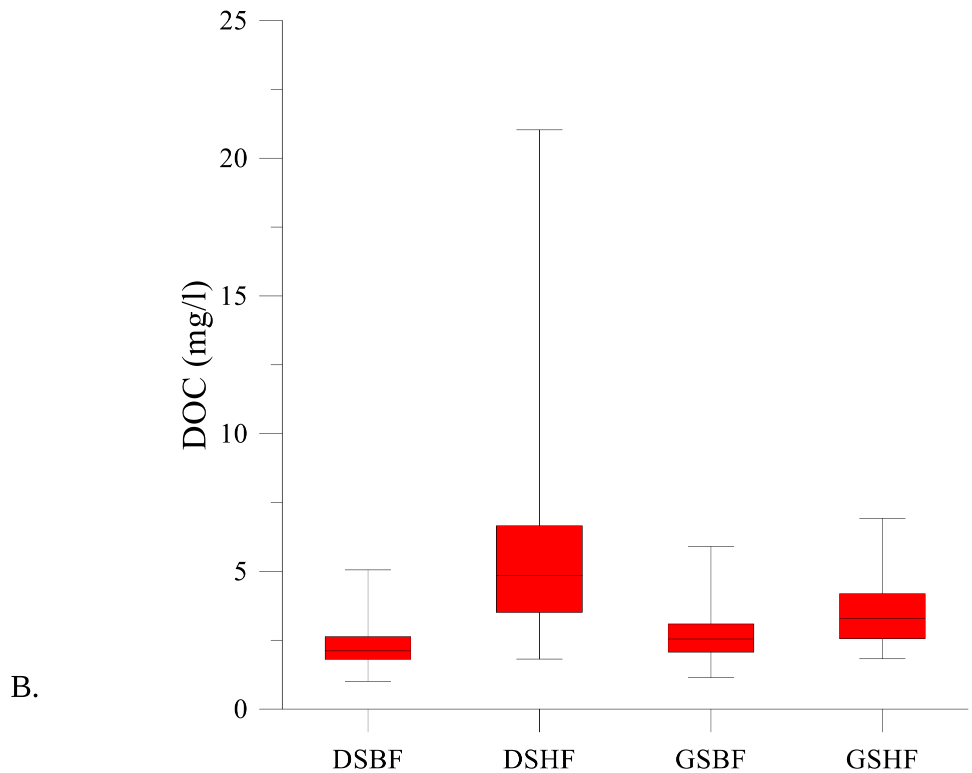
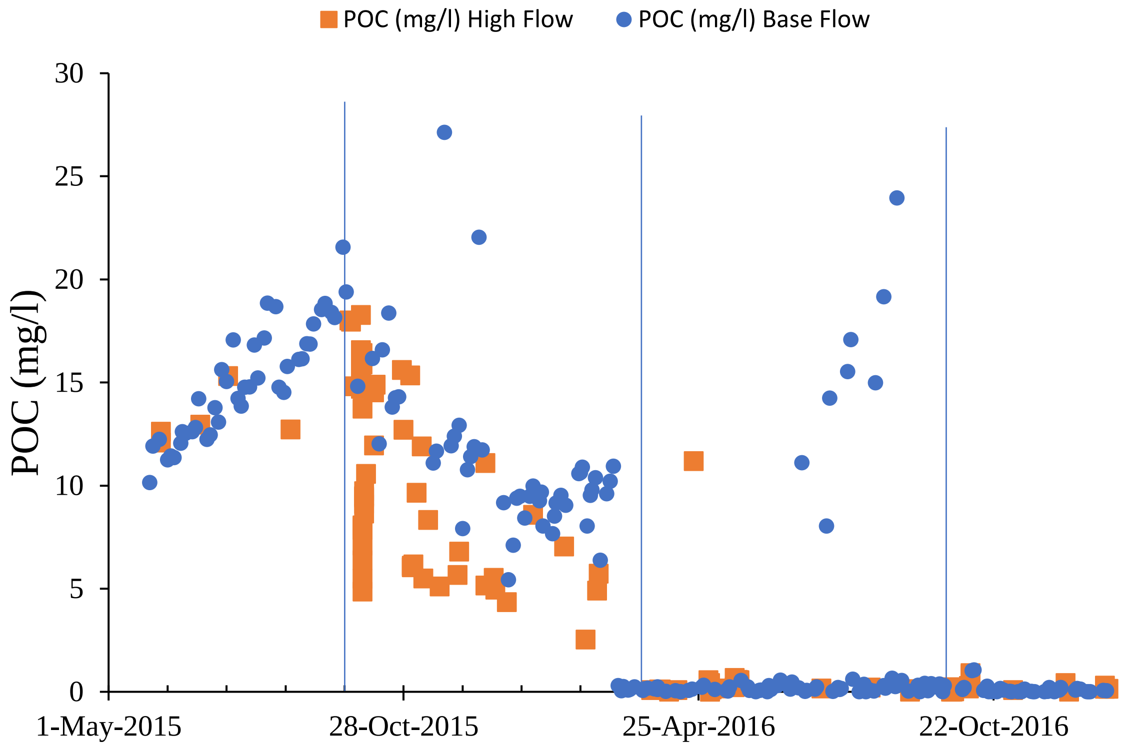


Figure 39: (A.) Scatter plot of MC5 stream's DOC concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's DOC concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

Stream water POC concentrations mirrored the TOC concentration. It showed a seasonal trend with gradual increasing trend from the time period of growing season of water year 2015 transition to dormant season of water year 2016 and a decreasing trend from the transition from dormant season of water year 2016 (Figure 40). This trend is supported by the supply of particulate organic material to the stream water during the autumn months. As seen in the case of the TOC concentrations, the POC concentration ranged from approximately 5 mg/l to 20 mg/l during the growing season of 2015 and dormant season of 2016, but then there was a sudden decline the POC concentrations from March 2016 and mostly remained under 2 mg/l with few exceptions. This decline which was observed in the POC concentration was in line with the time period of the initiation of the land clearing activity in the eastern part of watershed during March 2016. The average POC concentration post March 2016 was 1.06 mg/l, whereas prior to land clearing, the average POC concentration was 11.95 mg/l. The land clearing activity drastically reduced in inflow of the particulate plant material in the stream, thus reducing the POC concentration by an order of magnitude. Further, the POC concentration of high flow was generally less as compared to the base flow concentrations prior to the initiation of the land clearing activity, but after March 2016 this trend was reversed ((Figure 40 A). The POC concentration was approximately 77% of TOC concentration before the land clearing activity, but after that it decreased 87% and was approximately 10% of TOC concentration.

The yield (kg/ha/cm) of POC was higher by 96% in the dormant season 2016 as compared to the growing season of water year 2016 (Table 22). The mass balance analysis showed 49% retention of POC during the growing season 2016 as compared to the atmospheric inputs (Table 23).

A.



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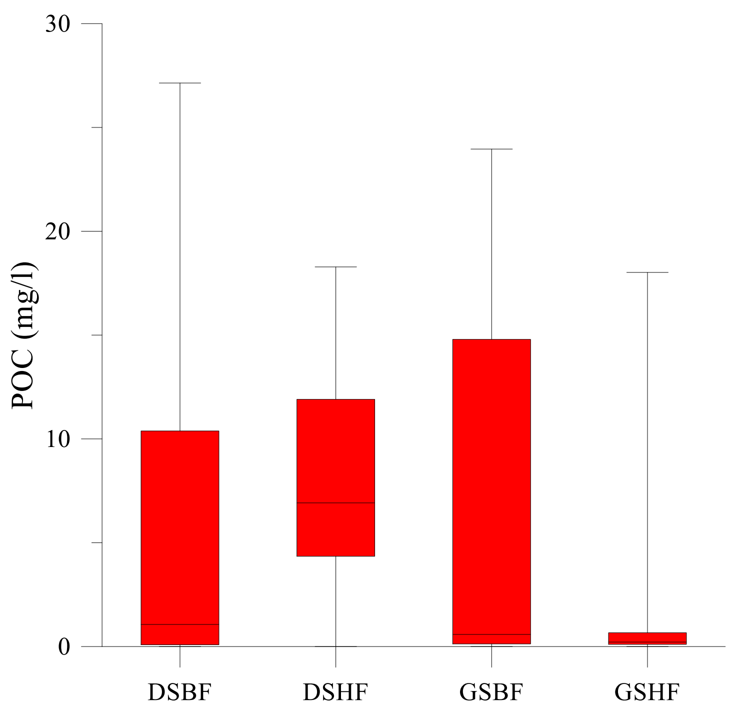

Figure 40: (A.) Scatter plot of MC5 stream's POC concentrations from May 26, 2015 to December 31, 2016; (B.) Box-whisker plot of MC5 stream's POC concentrations from May 26, 2015 to December 31, 2016 for DSBF, DSHF, GSBF and GSHF

7. Summary and conclusion

The objective of this project was to characterize the seasonal trends in hydrology, water quality and hydrochemical transport of sediments and nutrients of the Mecklenburg Catawba 5 (MC5) watershed. The MC5 watershed is located in the SE Piedmont and is undergoing land-use conversion from agricultural and open pasture to suburban housing. This watershed is part of the larger McDowell Creek watershed, which drains into the Mountain Island Lake drinking water reservoir. The first and second order streams originating from the watershed were restored as per the natural channel design approach and a riparian zone was established before the initiation of suburbanization activity on the watershed.

To explore the seasonal trends in the hydrology, the monthly water balance of water year 2016 and 2017 was analyzed. For the analysis of seasonal trends in water quality, the concentration of 27 water quality constituents was analyzed from the high frequency water samples collected from the outlet of the MC5 watershed. The significant differences between the dormant and the growing season and their respective high flow and base flow for the water quality constituents was analyzed by a non-parametric one-way analysis of variance. The hydrochemical transport for the dormant and growing season for the water year 2016 and the mass balance of the growing season 2016 was computed.

7.1 Seasonal difference in hydrology

The hydrology of MC watershed for the water year 2016 and 2017 reveal seasonal difference and increases the probability of rejection of the null hypothesis. The water balance analysis of hydrology of the growing and dormant seasons of the two water years, 2016 and 2017, show consistency in the runoff coefficient of the two dormant seasons (approximately 0.23). The growing season of water year 2017 was the wettest and received 64 % more precipitation than the previous growing season and resulted in 88 % rise in the runoff coefficient. The field measurements of soil moisture and shallow ground water levels showed deficits in the growing seasons and surplus in the dormant seasons, and support the potential evapotranspiration trend, which is 55% higher in the growing season as compared to the dormant season. The overall evapotranspiration, if calculated as the difference between precipitation and surface runoff, was 83 % and 82 % with respect to precipitation for the water years 2016 and 2017, respectively. Overall, the runoff coefficient was 0.17 and 0.18 for water year 2016 and 2017, respectively. Studies conducted in various Piedmont watersheds have shown that, a typical urbanized watershed with 20% impervious surface has runoff coefficient of 0.33, with 44% impervious surface has runoff coefficient of 0.42 and forested watershed has runoff coefficient of 0.21 (Boggs et al 2013). In comparison to the long-term Beaver Dam Creek watershed study (2003-2012) in SE Piedmont, the forested watershed BD1 showed annual runoff coefficient range from 0.11 to 0.27, with an average of 0.17 (Allan et al., 2013).

7.2 Seasonal and flow specific trends in water quality constituents

The majority of the 27 water quality constituents of MC5 stream water analyzed for the period from May 26, 2015 to December 31, 2016 displayed seasonal and flow specific trends and increases the probability of rejection of the null hypothesis (Figure 41).

The growing season conductivity was 1.24 times higher than the dormant season conductivity. The HCO_3^-, Ca^{2+}, Mg^{2+}, and Na^+ ions showed abundance in the base flow of the growing seasons and are indicative of the recharge of the MC5 stream by groundwater during the growing season, with deeper groundwater of relatively more residence time recharging the stream towards the end of the growing season. K^+ showed a distinct seasonal trend, with peak concentrations observed in the transition period from the growing seasons and subsequent dormant season, but unlike the other cations, the K^+ ion concentration increased significantly with discharge (Likens et al., 1967). K^+ ion is a sensitive indicator of biological activity and is markedly reduced during period of plant growth and increased during vegetation dormancy (Likens & Buso, 2013). The long-term study in the Catoctin Mountain (1982-1993) also observed seasonal cycles of HCO_3^-, Ca^{2+}, Mg^{2+} ions concentrations, with peaks in the growing season and attributed that to the water-table residing below the regolith-bedrock interface (Rice & Bricker, 1995). The H^+ ion activity, SO_4^{2-} and Cl^- ions concentrations were significantly higher during the high flow of dormant seasons and indicate shallower hydrologic flow paths in the regolith.

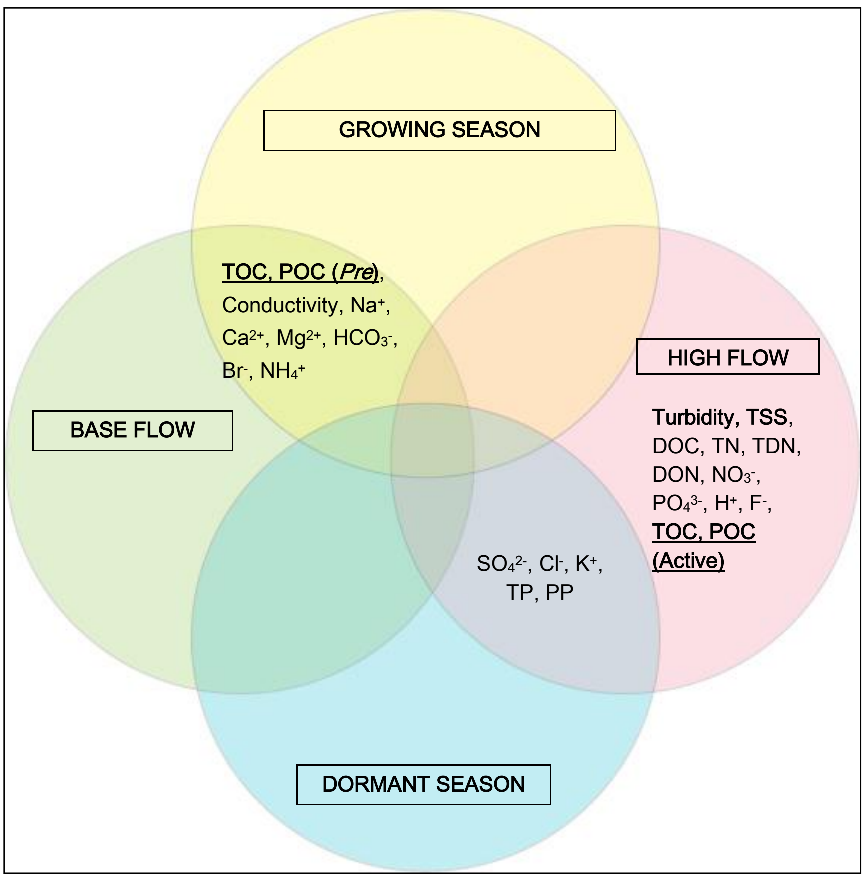

Figure 41: A Venn diagram display of significant difference in concentration between seasons and discharge condition. Grouping depict significantly higher concentration. TOC and POC are displayed twice, because of significant change in concentration observed during pre and active construction. TDP, DOP and PN show variability during active-construction and therefore are not displayed.

The nutrients TOC and POC displayed significantly higher concentrations in growing season base flow for the pre-construction samples, but during active construction the TOC and POC concentrations were significantly higher in the high flow samples as compared to the base flow samples (Figure 41). The concentrations of TSS, DOC, TN, TDN, DON, NO_3^-, PO_4^{3-} and F^- were also significantly higher in the high flow samples compared to the base flow samples of both seasons. The nutrient concentrations of TP and PP were significantly higher in the dormant season high flow samples as compared to the growing season high flow and growing season base flow samples. Due to the variability observed in the TDP, DOP and PN concentrations during the active-construction period, these are not categorized. The significantly high concentration of Br^- and NH_4^+ observed in the growing season base flow period indicates increases in the rate of bromination (Leri & Ravel, 2015) and ammonification (Ladd & Jackson, 1982) of the soil organic matter in the watershed.

7.3 Hydrochemical transport of water quality constituents

The yield (kg/ha/cm) of 25 water quality constituents were computed for the dormant and growing season of water year 2016. The yield of all but four water quality constituents were higher in the dormant season as compared to the 2016 growing season. The four water quality constituents which display significantly higher yield in the growing season of 2016 were TSS, PN, TP and PP, and were 1.14, 3.00, 3.70 and 5.59 times higher in the growing season 2016 than the preceding dormant season 2016.

The mass balance analysis of the growing season 2016 showed retention of all water quality constituents except Ca^{2+}, Mg^{2+}, HCO_3^-, and Na^+ which showed 33, 12, 0.60 and 0.04 times higher net export from the MC5 watershed as compared to the atmospheric inputs as measured by bulk precipitation.

7.4 Comparison to the Beaverdam Creek Study

Table 24: Comparison of yield (kg/ha/cm) of MC5 watershed for Water year 2016 to the Beaver Dam Creek Forested Watershed 1 (2003-2012)

Water quality constituents	Annual loading for Water year 2016 (October 2015 to September 2016) (kg / ha / cm)	Beaver Dam Creek Study (BD1 Watershed: Forested) (2003-2012) (kg / ha / cm) (Allan et al., 2013)	
		Lower range	*Upper range*
TSS	3	1.3731	16.7871
DOC	0.1	0.0392	0.1720
TN	0.01	0.0028	0.0147
NO_3^-	0.006	0.0009	0.0101
NH_4^+	0.002	0	0.0007
TP	0.007	0	0.0074
PO_4^{3-}	0.0008	0	0.0010
Cl^-	0.08	0.0287	0.1825

As seen from Table 24, in comparison to the BDC forest watershed the MC5 watershed annual yield (kg/ha/cm) for most chemical constituents falls within the range found at the BD1 watershed. NH_4^+ yield was the exception with a 65 % lower yield from BD1 than that observed at the MC5 watershed. The NH_4^+ ion concentration was generally below 0.3 mg/l for MC5 stream with significantly high concentrations in the growing season base flow as compared to dormant season base flow of water year 2016. Also, notable was the TP yield from the MC5 watershed, which was towards the higher range of that observed for the BDC forested watershed.

The NO_3^- ion concentration for the study period was below 4 mg/l except during the high rain event in October 2015. The NO_3^- ion concentration ranges from 0 to 6 mg/l for most of the urban areas across the US (Boggs et al. 2013). The concentrations of bromide in surface waters are a concern because this stream contributes to the drinking water reservoir and thus the treatment can produce brominated organics which are dangerous disinfection by-products with adverse impact on human health (Southern Environmental Law Center, 2017). The Br^- ion concentration was below 0.05 mg/l for the majority of water samples except during the end of growing season 2015 and flushing of Br^- ions by the high flow event of October 2015 lead to 4 times higher concentration (0.21 mg/l).

7.5 Initial impacts of construction

As per the watershed survey, it was in March 2016 that the land clearing on the eastern region of the watershed was initiated, from where the first order stream (Tributary East) of the watershed originate. The drainage area of the TE is 82 acres (33.18 ha) (Estes Design Inc. & Mid-Atlantic Mitigation LLC, 2009) and constitutes approximately 14 % of the total watershed area.

The turbidity of the dormant season 2016 was less by 79% as compared to the following growing season 2016, during which land clearing was initiated. TSS showed growing season 2016 yield (kg/ha/cm) more by 13% compared to the preceding dormant season 2016. The mean of TSS was 35.85 mg/l (± 78.83) prior to construction activity and it was 88.69 mg/l (± 320.14) after the initiation of construction activity. The TSS yield in the growing season of water year 2016 was 3.40 kg/ha/cm. In comparison, the Beaver Dam Creek Forested Watershed # 1 TSS yields ranged from 1.37 to 16.79 kg/ha/cm for the study period 2003 to 2012.

The mean of turbidity was 46.39 NTU (± 73.75) prior to construction activity and it was 129.66 NTU (± 422.32) after the initiation of construction activity. The allowable turbidity level under NC surface water quality guidelines is 50 NTUs for non-trout sustaining surface waters (NCDENR, 2007). The BD1 showed turbidity range from 87 NTU to 5403 NTU during the study period 2003-2012.

A distinct variation was observed in the post clearing concentrations of TDP, DOP, PN, TOC and POC, from March 2016 onwards. From the period from March 2016 to December

2016 the TDP and DOP concentrations showed a distinct variability and an increasing trend. The average concentration of TDP and DOP was 0.03 mg/l (± 0.01) and 0.02 mg/l (± 0.01), respectively prior to construction activity. After the initiation of construction activity, the average concentration of TDP and DOP was 0.04 mg/l (± 0.01) for both of these water quality constituents. The PN concentration was 0.01 mg/l (± 0.12) prior to construction activity and it was 0.04 mg/l (± 0.06) after the initiation of construction activity. There was a sudden decline in the TOC concentrations attributed to a decline in POC from March 2016. The land clearing activity drastically reduced in inflow of the vegetation derived material in the stream, thus reducing the TOC and POC concentration by approximately two times. The average concentration of TOC and POC was 15.31 mg/l (± 3.79) and 11.96 mg/l (± 4.27), respectively prior to construction activity. After the initiation of construction activity, the average concentration of TOC and POC was 4.12 mg/l (± 3.95) and 1.06 mg/l (± 3.66), respectively for these water quality constituents. Also, the TOC and POC concentration during high flow periods was generally less as compared to the base flow concentrations prior to the initiation of the land clearing activity, but after March 2016 this trend was reversed. This trend in the flow concentrations indicate the change in the supply and transport mechanism of plant derived material in the stream. Further, the disturbance caused by the land clearing activity potentially increased erosion, aiding the leaching of legacy sediments from past agricultural activities in the stream water, and causing an increase in the flux in TDP, DOP and PN concentrations.

The extension of this study will reveal changes in the hydrology and biogeochemical states of the watershed as this watershed is rapidly changing in land use. Also, as the land use change stabilizes, this study will address the effectiveness of the stormwater best management practices and low impact development landscape designs implemented in the watershed.

8. References

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