DETERMINING SOURCES OF DISSOLVED ORGANIC CARBON AND NUTRIENTS IN AN URBAN BASIN USING NOVEL AND TRADITIONAL METHODS

A Thesis

by

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ABSTRACT

Water quality in urban ecosystems is sensitive to localized disturbances potentially affecting those mechanisms which influence nutrient cycles. The Carters Creek Basin has been reported to have elevated concentrations of dissolved organic carbon (DOC). In combination with high terrestrial nutrient export from non-point sources and point source effluent discharge, this has been suggested to contribute to *E.Coli* recovery and regrowth. Spatial identification of loading "hot-spots" or locations of elevated nutrient concentrations of non-point, terrestrial sources may provide critical information necessary for appropriate mitigation efforts and watershed management. This study used traditional and novel methods for source tracking nutrients and dissolved organic carbon in small urban and rural watersheds in Brazos County, Texas. A nested watershed approach allowed identification of problem areas of nutrient loading. A novel cost-effective technique using diffuse reflectance near-infrared spectroscopy was used to identify sources of DOC. Monthly stream sampling was conducted at 12 sites from 2012 to 2013.

Impacts of human activity on landscape features determining source pathways for nutrient retention, transport, and conversion were identified in this study. Higher nitrate-N (0.12-22.8 mg L^{-1}), orthophosphate-P (0.11-3.60mgL^{-1}), and DOC concentrations (18.6-68.1 mg L^{-1}) were found across the watershed than in 2007. Factors such as increased erosion, sodic soil dispersion, land use, and flow conditions were

identified as possible causes for increased carbon (C), nitrogen (N) and phosphorus (P) observed in the basin.

This study supported the use of near-infrared spectroscopy to elucidate watershed sources of carbon. The major sources of DOC into the Carter Creek basin watersheds were leachate from soil and turfgrass. Rural subwatersheds had less complicated source signatures than their urban counterparts. Urban impervious runoff signatures also clustered with stream water signatures, especially during high flow in October and September. These results indicate that specific vegetation such as turfgrass used for landscapes in urban watersheds coupled with sodic irrigation may alter traditional nitrogen, phosphorus and carbon cycling in urbanizing watersheds. Spatial source tracking will enable efficient pollution mitigation and protect water quality as a result of this study.

For Neha, who taught me life isn't about hiding from the storm, but about learning to dance in the rain.

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NOMENCLATURE

CCB	Country Club Branch
CFU	Coliform forming units
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DR-NIRS	Diffuse-reflectance rear-infrared spectroscopy
DDW	Distilled deionized water
EC	Electrical conductivity
GIS	Geographic information systems
NLCD	National Land Cover Database
NH_4-N	Ammonium-N
NO_3-N	Nitrate-N
PO_4-P	Orthophosphate-P
TCEQ	Texas Commission on Environmental Quality
TDN	Total dissolved nitrogen
WSSL	Watershed spectral source library
WWTP	Waste water treatment plant

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 IMPORTANCE OF WATERSHED SCALE DISSOLVED ORGANIC CARBON DYNAMICS

It has been long understood that carbon dynamics are an integral component of the health and functioning of ecosystems at all scales (Schlesinger and Melack 1981; Kindler et al. 2011). A resolve to understand the carbon cycle at landscape and regional scales has therefore been highlighted as requiring robust measurements and estimates of exports of organic carbon in streams and rivers (Aitkenhead-Peterson et al. 2007). Dissolved organic carbon (DOC) plays an important role in the global carbon balance (Schlesinger et al. 1981; Meybeck 1982; Hope 1994); particularly through the movement of carbon across landscapes (Canham et al. 2004). It is also a major pathway of element cycling (Kalbitz et al. 2000). Siemens (2003) argued that the gap between land and atmospheric based estimates of carbon uptake could be explained by the leaching of dissolved inorganic and organic carbon from soils. Kindler et al. (2011) highlighted authors who supported Siemens (2003) argument claiming that the consideration of inland waters as components of terrestrial carbon budgets was necessary to assess the carbon cycle at the landscape scale. Therefore, understanding of soil and riverine carbon dynamics at smaller scales can be beneficial to interpreting carbon dynamics when conducting assessment of net ecosystem carbon balances.

The effects of DOC can be both detrimental and essential to life in delicate riverine systems. Canham et al. (2004) noted that differences in DOC concentrations in aquatic ecosystems are associated with variation in important physical, chemical, and biological properties. An essential substrate for aquatic heterotrophs, DOC sustains life and is a source of energy for microbial activity in stream waters (McKnight et al 2001; Hessen, 1992). Excess DOC on the other hand, can mobilize soluble metals (Driscoll et al. 1988), release pesticides from particulate matter in suspension (Worrall et al. 1997) and limit penetration of solar radiation (Canham et al. 2004). Detrimental effects of DOC have also been investigated in human-aquatic interactions. For example, reactions of DOC with disinfectants during drinking water treatment processes result in the formation of carcinogenic by-products, namely trihalomethanes. Trihalomethanes have frequently been cited as a serious concern for streams with elevated concentrations of organic carbon (Galpate et al. 2001; Westerhoff and Anning 2000; Chu et al. 2002). Although the literature is well versed in the significance of DOC to natural ecosystems such as forested or rangeland; the concentrations, sources, quality, and functions of carbon in disturbed urban ecosystems are poorly understood in comparison to their less disturbed native counterparts (Steele et al. 2010). In light of rapid urbanization in many parts of the world, greater attention needs be drawn to the changing dynamics of DOC in transitional as well as urbanized watersheds.

Most studies to date have focused on soil carbon dynamics in temperate regions and forested biomes. (see review of Kalbitz et al. 2000). Aitkenhead and McDowell (2000) illustrated this focus on temperate and forested biomes summarizing data on exports of carbon from a number of biomes globally. They demonstrated that temperate watersheds have dominated aquatic DOC research relative to sub-tropical and tropical watersheds. Aitkenhead et al. (1999) also demonstrated the significance of watershed scale on DOC concentrations. Spatial scale of investigation is therefore important to the concentration and type of organic compounds entering surface waters. This warrants study into the carbon dynamics of small watersheds, particularly mixed land use watersheds. Few studies have explicitly engaged with tracking landscape sources of organic carbon in urban watersheds although many studies have focused on the effect of landscape on DOC concentrations and exports in rural or minimally disturbed watersheds. For example Canham et al. (2004) studied a spatially explicit model of lentic surface water DOC concentrations in 428 watersheds in the Adirondacks of upstate New York. The authors found land cover and precipitation volumes strongly influenced DOC exports, with forested areas contributing a significant portion of measured DOC. Aitkenhead and McDowell (2000) investigated the export variability of riverine DOC and found the C:N ratio in biome soils influenced exports which ranged from less than 3 to greater than 130 kg ha^{-1} yr^{-1}. Further studies within temperate forested and range biomes confirmed that watershed soil C:N could be used to predict DOC exports (Aitkenhead-Peterson et al. 2005; Aitkenhead-Peterson et al. 2007).

1.2 DISSOLVED ORGANIC CARBON IN URBAN STREAMS

Those studies that have given attention to the effects of urbanization on DOC have mainly dealt with concentrations and characteristics of organic carbon in surface waters (Sickman et al. 2007; Westerhoff and Anning 2000; Hook and Yeakley 2005) rather than exports and sources. Influences of variables such as hydrologic regimes (Hook and

Yeakley 2005), land management practices (Wright et al. 2008; Aitkenhead-Peterson et al. 2009; Petrone 2010; Aitkenhead-Peterson and Cioce 2013), presence of wastewater treatment facilities (WWTF) (Westerhoff and Anning 2000; Aitkenhead-Peterson et al. 2009), land use (Steele et al. 2010), landscape vegetation type (Pannkuk et al. 2011), on DOC concentrations and exports in soil and surface water have been investigated. Evans et al. (2007) established climate change as one of many anthropogenic drivers of elevated DOC flux through impacts on soil destabilization. Nutrient retention on asphalt surfaces has also been suggested as a significant potential DOC flux in urban ecosystems (Hope et al. 2004).

Some studies however have found contradictory results to their initial predictions. For example, Sickman et al. (2007) found urban contributions to total organic carbon (TOC) to be 10%, with higher DOC concentrations (60%) attributed to WWTFs than non-point runoff (40%). A study by Aitkenhead-Peterson et al. (2009) in urban watersheds in South-Central Texas reported that watersheds receiving WWTF effluent did not display significantly higher concentrations of DOC relative to watersheds without WWTFs and that high sodium irrigation water was the primary control on DOC concentrations in their urban streams. Hook and Yeakley (2005) predicted lower DOC flux to streams during storm flow than in baseflow in a small urban watershed in Oregon due to dilution effects of rapid runoff; however their results showed increased DOC concentrations during storm flow which they attributed to remnant riparian zones in the watershed. Petrone (2010) reported higher DOC concentrations in urban relative to rural watersheds in a study of the Swan-Canning

River in Western Australia. The relatively small number of studies on urban streams demonstrates the dearth of in-depth understanding of carbon dynamics in urban watersheds. Although these urban stream studies have provided a valuable insight into factors driving DOC concentrations and export in urban watersheds, debates over dominant factors such as flowpaths and point source sewage effluent driving increased DOC concentrations retain prominence in the literature.

1.3 URBAN SURFACE WATERS AND ASSOCIATED NUTRIENTS

Urbanization has been shown to significantly alter typical loadings of nutrients, metals, pesticides, and other contaminants to streams (Hope et al. 2004; Steele et al. 2010). A greater concentration of impervious surfaces together with soil disturbance and compaction increase surface runoff and alter hydrological flowpaths (Paul and Meyer 2001). Recent work on surface waters in urban watersheds has focused on nitrogen (Dahlen et al. 2000; Barnes and Raymond 2010) and phosphate cycling (Smil 2000). Polyaromatic hydrocarbons (PAHs) and polychlorinated biphenols (PCBs) have also received increasing attention in the literature (Van Metre et al. 2009).

1.4 SOURCE TRACKING STREAM DISSOLVED ORGANIC CARBON, NITROGEN AND PHOSPHORUS

Source tracking and composition analysis would be useful tools for managing water quality in impaired watersheds. Determination of load variance explained by different watershed components assists in the effective implementation of properly targeted management measures. Currently, methods for source tracking of nitrates (Barnes and

Raymond 2010; Burns et al. 2009) and *E.coli* (Field and Samadpour 2007; Carlos et al. 2011; Kalin et al. 2010) are most common in the literature. Other methods of source tracking carbon and nutrients in watershed streams include simple regression analysis (Aitkenhead et al. 1999; Aitkenhead-Peterson et al., 2005, 2007, 2010), dual isotope analysis (Barnes and Raymond 2010; Burns et al. 2009), fluorescence (McKnight et al. 2001; Spencer et al. 2010), and neural networks (Clair and Ehrman 1998; Aitkenhead et al. 2007). Limited studies have attempted source tracking of organic carbon in urban watersheds. Given the importance of DOC in aquatic systems, a further investigation of source tracking organic carbon is needed.

DOC export analysis presents valuable insight into sources of DOC in watersheds. Although gradients of DOC concentrations can be measured with current analytical techniques, coupling of specific signatures unique to particular sources presents a great challenge (Westerhoff and Anning 2000). Empirical modeling with simple linear regression analysis has been used by Kortelainen et al. (1997) to estimate dissolved organic matter (DOM) exports as determined by relationships of various watershed attributes. A limitation of this type of analysis is that it is only as powerful as the resolution of the data used. In rapidly urbanizing landscapes where land use is highly variable, the strength of such analysis is diminished. Neural networks are another commonly applied method in analysis of water resource phenomena. Neural network analysis creates mathematical algorithms to evaluate a number of input and output variables and determine their relationships (Clair and Ehrman 1998; Aitkenhead et al. 2007). These neural network models require location specific adjustments to account for local hydrology and are affected by a vast number of watershed soil characteristics (Aitkenhead et al. 2007) and are therefore limited in their spatial transferability. Furthermore, neural networks indicate potential sources; and do not provide details about unique DOC sources. Carbon dating methods are another technique which was applied by Sickman et al. (2007) to Californian streams to determine the age of nonpoint source DOC. Although useful, such models are limited by their inability to identify specific components of dissolved compounds with sufficient detail to aid watershed management.

Current carbon source tracking methods resolve sources by drawing comparisons between the composition of water samples or its particulates and watershed sources (Christopherson and Hooper 1992; Hinton et al. 1998; McKnight et al. 2001; Hooper 2003; Stedmon et al. 2003; Lafreniere and Sharp 2004; Inamdar et al. 2011). Due to the complex nature of DOC molecules and its potential transformations and interactions along hydrological flowpaths, quantification from specific source areas is difficult suggested Bishop et al. (1994). As such, current carbon source tracking techniques have attempted identification of end members only through the use of indirect measurements. Early work in this field focused on identifying DOC sources through hydrographic separation. DOC concentrations were resolved by identifying the sources of water contributing DOC to a common pool. Much research has demonstrated the utility of such a technique in distinguishing water sources from baseflow, groundwater, deep groundwater, shallow riparian groundwater and so forth (Christopherson and Hooper 1992; Hinton et al. 1998; Hooper 2003). Identification of the principal hydrologic components of stream water in these studies has allowed for predictions of DOC concentrations. Modeled DOC concentrations, when paired with measured concentrations, have provided information about the origins of carbon export and processes affecting it within a watershed. Pioneers of this field, Christopherson and Hooper (1992) applied end-member mixing analysis (EMMA) to determine the number of end-members, or contributing sources based on application of multivariate statistical techniques. Although EMMA is not exclusively applicable to hydrologic source separation, it has widely been applied for its use. Watershed chemistry has often been modeled with EMMA using various tracers such as DOC. Mixing models solve simultaneous mass balance equations for tracers using statistical tools such as principal component analysis (PCA) (Hooper 2003). Though this modeling approach has achieved relative success in spatial and temporal separation of relative contributions from source areas (Burns et al. 2001), it lacks the ability to exactly identify sources.

Chemical composition of DOC for indirect measurement of contributing sources is another frequently utilized approach. Researchers tested the feasibility of using DOC quality and other runoff parameters to specify contributions from specific source areas in a riparian zone in a catchment in northern Sweden (Bishop et al. 1994). Sources were identified by testing the ratio of humic:fulvic components in solutions and molecular size distribution using gel filtration. UV-Visible absorbance has also been applied in measuring the quality of DOM (Inamdar et al. 2012). Specific UV absorbance (SUVA 254) indicated composition differences between the watershed sources sampled in the study. SUVA 254 is a measure of humic substances in water sources and hydrologic separation was combined with chemometric statistical analysis to associate measured SUVA 254 parameters to sources. The recent trend of extracting quantitative information from proximal remote sensing techniques is on the rise and is an inexpensive and faster technique for watershed source derivation than lengthy laboratory procedures and analysis such as assays (Geladi and Dabakk 1995).

Spectrofluorometric techniques have proven useful in identifying the character of surface waters from which sources can be elicited (McKnight et al. 2001; Stedmon et al. 2003; Lafreniere and Sharp 2004; Inamdar et al. 2011). Differences in chemical composition distinguished using optical indices have allowed deductions to be made about relative source areas. For example, terrestrial vegetation DOC has a unique chemical signature; differing from that of soil DOC which has microbial origins. McKnight et al. (2001) pioneered a technique using excitation and emission matrices (EEMs) of fulvic acids. The study demonstrated the fluorescence index; the ratio of emission intensity at 450nm to 500nm for an excitation of 370nm, which allowed for differentiation between microbial and vegetation DOC sources. Other studies (Inamdar et al. 2011; Lafreniere and Sharp, 2004) have indicated similar results due to the aromatic nature of humic acids. Terrestrially derived sources contain higher concentrations of humic acids extracted from vegetation and the upper layers in the soil profile (Bishop et al. 1994). Therefore stream samples with higher concentrations of humic materials are thought to be of terrestrial origin.

Since the pioneering work of McKnight et al. (2001), a suite of optical indices and tracers have been used as indices for DOC origin across multiple environmental conditions. Interpretive parameters include the wavelength of peak fluorescence (λFmax) (Lafreniere and Sharp, 2004), 3D fluorescence of Na^+ and SO_4^{2-} (Katsuyama and Ohte, 2002), %C5, %C3 and %protein-like fluorescence (Inamdar et al. 2012). Although a host of information can be inferred from such methods of DOC characterization, little direct proof of which terrestrial source materials end up in the aquatic systems exists in the literature.

Stable carbon isotopes have been used to provide important information about sources and ages of organic carbon (Peterson and Howarth 1987; Kwak and Zedler 1997; Raymond and Bauer 2001). Mass balance approaches that quantify ^{13}C and ^{14}C ratios have been proven to differentiate between allochthonous (from watershed) and autochthonous (in stream) contributions and type of plant material (Cioce et al. in review; Raymond and Bauer, 2001). A number of studies have incorporated isotope analysis in investigations of carbon sources in two and three source mixing models in estuarine (Peterson and Howarth 1987; Kwak and Zedler 1997), riverine (Raymond and Bauer 2001) and oceanic (Bauer et al. 2001) environments. The relative ratio of isotopic signatures found in aquatic consumers was initially utilized to elucidate sources of carbon from particular geographic areas in aquatic systems (Peterson and Howarth, 1987). Researchers have also used isotope signatures of nitrogen and carbon in consumers for indirect measurement of organic matter transport to salt-marsh estuaries in Georgia (Peterson and Howarth 1987). Source determination in this study was carried out through comparison of isotopic signatures in source materials to those in end-members. Another coastal study found material derived from offshore, estuarine, and primary production to contribute to the DOC pool (Raymond and Bauer, 2001). Isotopic analyses however can be sparse and inconclusive. Overlap in ^{13}C isotopic values of several major sources of DOC within river and estuarine systems is the primary limitation to this technique (Cioce et al. in review). Furthermore, a key assumption of the conservative nature of isotopes from source to sample location remains untested. Preliminary research has shown preferential consumption of ^{14}C by bacteria where isotope ratios were altered spatially and temporally (Raymond and Bauer, 2001). These limitations suggest isotope mass balance approaches are still in its infancy and cannot be conclusively applied to indicate individual sources of DOC.

1.5 USES OF NEAR INFRARED SPECTROSCOPY IN ECOLOGICAL STUDIES

Near infrared spectroscopy (NIR) is an optical analytical technique that has been widely used in agriculture, paper, food, manufacturing, and pharmaceutical industries for analyses of product composition and function. Near infrared spectroscopy describes the molecular composition of organic material in a sample and is based on the vibrational patterns and absorption of near infrared radiation by bonds (specifically C-H, N-H, and O-H) in the material of interest (Nilsson et al. 1996; Foley et al. 1998; Bokobza 2002; Perrson et al. 2007). These bonds tend to have "high vibrational frequencies" in the near infrared region (780 nm to 2500 nm), allowing the molecular composition of organic material to be determined (Nilsson et al. 1996; Korsman et al. 2002). Typically, a linear relationship between absorbance and concentration (following the Beer Lambert Law) is shown in most biological and agricultural applications (Nilsson et al. 1996). The spectral signatures derived are then usually combined in a statistical model which may be used to predict the molecular composition of unknown samples (Foley et al. 1998). The accuracy of the NIR spectroscopy model depends on the reference and calibration data, but NIR spectroscopy is “often more precise” than laboratory assays (Geladi and Dabakk 1995; Foley et al. 1998).

Near infrared spectroscopy has also been used in a limited capacity in ecological studies (Perrson et al. 2007), but there is great potential for its use in environmental monitoring (Foley et al. 1998). Most work so far has been on its use for determining plant lignin and cellulose concentrations (McLellan et al. 1991; Bolster et al. 1996), soil carbon and nutrient concentrations or enzyme function (Dalal and Henry 1986; Ben-Dor and Banin 1995; Cozzolino and Moron 2003) or soil physical properties (Bogrekci and Lee 2005; Viscarra Rossel et al. 2006, Waiser et al.2007; Viscarra Rossel et al. 2009). The limited use of NIR in water research has focused on particulate material (Malley et al. 1996; Dabakk et al. 2000; Korsman et al. 2002; Perrson et al. 2007). For example, NIR spectroscopy was used to predict lake water chemistry (total organic carbon, total phosphorus, and pH, among other constituents) in Sweden based on NIR analysis of seston collected on filters (Dabakk et al. 2000). Malley et al. (1996) used NIR to determine carbon, nitrogen, and phosphorus in both suspended and particulate matter in lake water in Ontario. A study in paleolimnology used NIR spectroscopy to reconstruct sediment and water chemistry in Sweden (Korsman et al. 2002), where it was found that NIR spectroscopy performed better than chemical and diatom analyses in a study examining epilithic material in streams impacted by mining (Perrson et al. 2007). More recently, Collins et al. (2013) examined watershed source particulates using NIR spectra to determine those particulates affecting salmon spawning gravel in Great Britain and reported that C sources from decaying vegetation, septic tanks and farm manures negatively impacted salmon spawning gravel.

1.6 CONCLUSIONS

In conclusion, there is much speculation in the literature about carbon dynamics in surface waters in general and as yet, little information on carbon dynamics in urban watersheds. Current characterization and source tracking methods lack sufficient detail to provide qualitative analysis of watershed DOC sources. A primary limitation is the assumption of molecule transformations from source (the watershed) to sink (the stream) which has deterred many researchers because of the complexity of potential changes in the DOC molecules. The majority of studies, particularly those using simple regression analyses of land use and DOC concentrations and export, do not take biological or chemical transformations into account when linking surface water DOC to terrestrial sources. Research suggests that DOC is a substrate for microbes and therefore the molecule becomes incorporated in microbial biomass (immobilized) or is mineralized. DOC in vegetation extracts is between 31 and 79% biodegradable by microbes (McDowell et al. 2006; Cioce and Aitkenhead-Peterson in review). DOC in soil extracts or solution ranges between 2 and 77% biodegradable (McDowell et al. 2006; Cioce and Aitkenhead-Peterson in review). DOC in surface waters is between 1 and 30% biodegradable (Gremm and Kaplan 1998; Moran et al. 1999; Wiegner and Seitzinger 2001; Wiegner et al. 2006; Wiegner and Tubal 2010; Cory and Kaplan 2012; Cioce et al. in review) so it would appear that the DOC that makes it to surface waters is, for the most part, refractory and therefore it is possible that this refractory DOC can be characterized to specific watershed sources. To address this issue, small catchments such as the Carters Creek basin, south-central Texas, USA offers a finer scale watershed approach in source tracking methodology.

1.7 OBJECTIVES OF RESEARCH

Objective 1: To examine DOC, N and P concentrations in sub-watersheds of a nested urban basin and their relationship with land use.

a) Examine the effect of land use on high and low flow on stream C, N and P concentrations.

b) Examine the effect of hot and cool seasons on stream C, N and P concentrations.

c) Determine if DOC, N and P concentrations in the nested sub-watersheds are a result of dilution or addition.

Hypotheses to be tested:

H1: Stream pH, electrical conductivity, DOC, N and P concentrations will be significantly higher during high flow conditions because of storm water runoff from the watershed.

H2: Stream DOC, N and P concentrations will be significantly lower during the hot season due to microbial and plant uptake limiting available watershed sources.

H3: Stream water DOC, N and P will be positively correlated with urban land use and negatively correlated to rural or native land use because nutrient cycling is tighter in undisturbed ecosystems.

Objective 2: To examine, using principal component analysis and hierarchical cluster analysis the efficacy of determining stream water DOC sources using DR-NIRS.

a) Collection of watershed source materials, their extraction and collection of spectral signatures to produce a watershed source spectral library (WSSL).
b) Quantify dominant sources of DOC in the nested stream set using principal component analysis (PCA) and hierarchical cluster analysis with Euclidean distance.
c) Determine the main terrestrial sources of DOC during high flow and low flow in a range of watersheds along an urban to rural gradient.

Hypotheses to be tested:

H1: Spectra of specific watershed source materials will cluster in logical groups.

H2: Stream spectra will cluster with the watershed source material with which it shares a common signature.

CHAPTER II

URBAN CARBON, NITROGEN, AND PHOSPHORUS DYNAMICS: A NESTED WATERSHED APPROACH

2.1 INTRODUCTION

Nutrients are key indicators of healthy surface waters. Excessive nutrients can have negative impacts on aquatic flora, fauna, and human health (Jones et al. 2001). Nitrogen (N) and phosphorus (P) are essential plant and microbial nutrients which can cause eutrophication of surface waters and lowered streamwater dissolved oxygen levels when present in abundance (Jones et al. 2001).

In urban streams, runoff from impervious surfaces coupled with high nutrient concentrations have been documented as causing physical and chemical and impacts on water quality (Paul and Meyer 2001; Steele et al. 2010). This increased runoff from altered hydrologic flow paths is largely due to a greater proportion of impervious cover; these are dominant in urban watersheds and the physical effects of this increased runoff is bank and bed scouring in streams. Chemical effects such as increases in salts, N and P are also commonly observed (Clinton and Vose 2006). Aitkenhead-Peterson et al. (2009, 2011) suggested that the quality of irrigation water used for irrigating open urban areas might be responsible for increased dissolved organic carbon (DOC) and nitrogen exports from areas such as golf courses, athletic fields, neighbourhood parks and residential gardens in Texas. Elevated concentrations of nitrogen and phosphorus were found in urban streams dominated by impervious surfaces (Jones et al. 2001; Hope et al. 2004).

The presence of waste water treatment plants (WWTP) (Carey et al. 2009) and combined storm sewer overflows (CSOs), and application of lawn care products in urban watersheds have also been shown to significantly alter stream water chemistry in comparison to undisturbed areas (Paul and Meyer 2001; Aitkenhead-Peterson et al. 2011). Due to the importance of carbon, nitrogen and phosphorus for aquatic and human health, further study of urban nutrient dynamics is warranted.

Nutrient availability and composition has been documented to effect bacterial regrowth in surface waters (McCrary et al. 2013). The authors determined that nitrogen and phosphorus contained in permitted sewage effluent discharge in conjunction with readily available DOC, nitrogen and phosphorus leached from the landscape provided ideal conditions for *E.coli* regrowth in surface waters downstream of point source discharge. Orthophosphate-P, nitrate-N, and dissolved organic nitrogen (DON) released from turfgrass and leaf litter were identified as significant predictors boosting *E.coli* regrowth in the urban watershed. The findings in the McCrary et al. (2013) study were significant under both low and high flow conditions warranting further examination of watershed nutrient loading.

Spatial approaches to the study of water quality emerged alongside the development of GIS (geographical information systems) technology (Wernick et al. 1998). Several studies have shown that land use within a watershed can explain water quality impairments (Hunsaker and Levine 1995; Wernick et al. 1998; Jones et al. 2001). Jones et al. (2001) tested various landscape metrics for their effect on N, P and sediment loadings to streams in the Mid-Atlantic region. They reported that the most important landscape variables in the models developed were the proportion of riparian forest and agriculture in sub-watersheds. Hunsaker and Levine (1995) also discovered landscape attributes influenced water quality at various spatial scales in nested-approach studies. The authors determined that watersheds in the Wabash River in southeastern Illinois and Lake Ray Roberts in north Texas demonstrated that landscape patterns such as the proportion of certain land uses were important for modeling water quality. Furthermore, both land use and land management practice effects were shown by Aitkenhead-Peterson et al. (2009, 2011) on DOC and N and P exports from both rural and urban landscapes. As such, land use alone cannot be the sole criteria for determining water quality in mixed-use watersheds containing urban centers and land management practices must also be considered.

The relationship between water quality and land use is highly variable and not fully understood. Water quality in urban, forested, and undisturbed streams responded to changes in landscape composition and stream discharge in headwater streams in the Southern Appalachians (Clinton and Vose 2005). In the Clinton and Vose (2005) study, forested streams with significant riparian buffers had consistently lower N and P concentrations than their urban counterparts which typically had no riparian buffers. Linear relationships between stream nutrients and watershed land use are not always found in watershed studies. For example, Wernick et al. (1998) were unable to determine a linear relationship between streamwater nitrate-N and land use in an urban-rural fringe watershed. Similarly Zampella et al. (2007) reported that the impact of land-use patterns, notably in agricultural and urban areas, was only useful to water quality models at a given threshold. For example, the authors found that a 10% altered land-cover in the Mullica River Basin in the New Jersey Pinelands produced a statistically significant increase in nitrate-N and nitrite-N concentrations. Greater land cover alterations of 10-19% and 40% also differed significantly from reference site water quality conditions. A study by Hunsaker and Levine (1995) suggested the transferability of metric studies relating water quality to landscape attributes was limited by biophysical settings of concerned watersheds. Given the complexity of relating landscape metrics to water quality, a nested-approach could aid in identification of critical nutrient loading areas or ‘hot spots’ of nutrient loading. Such information will be beneficial to water resource professionals in directing their resources and management efforts.

Carters and Burton Creeks are currently listed as impaired waterbodies for elevated bacterial levels on the Texas Integrated Report for Surface Water Quality 303(d) list. Carters Creek has been listed since 1999 and Burton Creek since 2006 (TCEQ 2012). Currently both streams have listed concerns for orthophosphate-P and nitrate-N according to the annual 2012 Texas Integrated Report-Water bodies with concerns for use attainment and screening levels (TCEQ 2012). Given these concerns over water quality in the Carters Creek basin, understanding patterns of N and P loading is essential to assisting rehabilitation efforts. The objective of this study was to apply a nested-approach to urban and urbanizing watersheds in the Carters Creek basin, a small sub-tropical oak savannah basin in south central Texas to identify causes of water quality impairments

2.2 MATERIALS AND METHODS

2.2.1 Site Description

The study was located within the Carters Creek basin situated in south-central Texas and within the cities of Bryan and College Station (Fig 2.1). Population of the Bryan/College Station metropolis was 228,660 in 2010 (US Census 2010). Dominant soils in the region are Alfisols underlain with marine clays (Aitkenhead-Peterson et al. 2009).

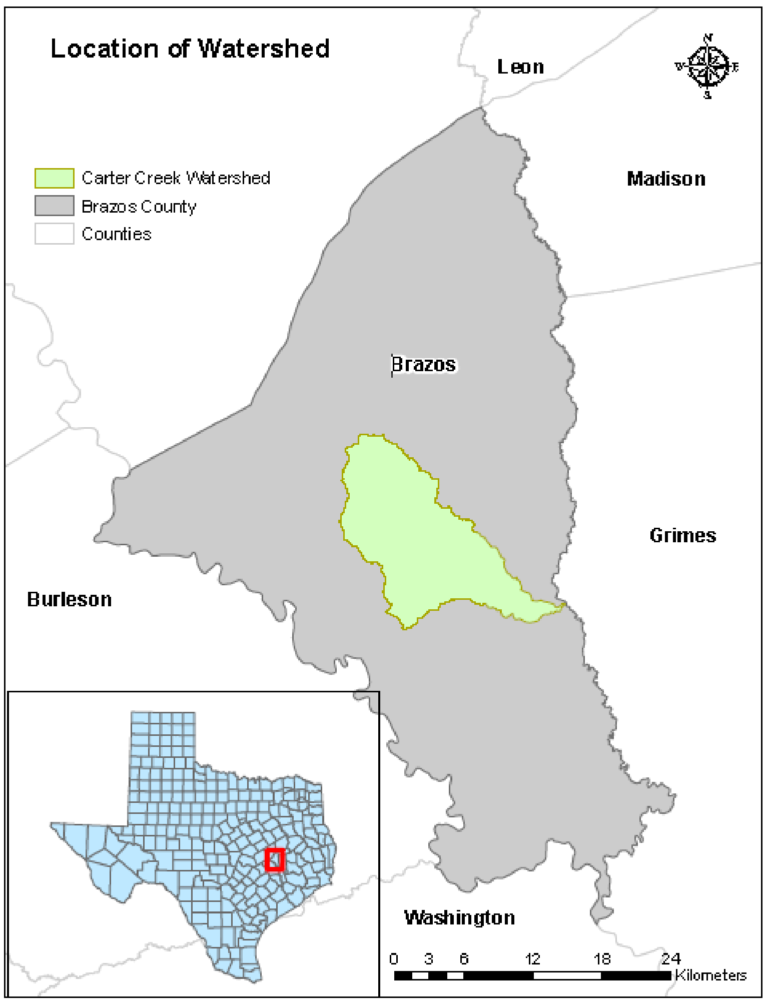


Fig. 2.1 Location of the Carters Creek basin study area within Brazos County, TX

The climate of Carters Creek basin is humid subtropical with a mean annual temperature of 20°C and an average annual precipitation of 992 mm (NRCS 1993). High intensity precipitation in short duration storm events occurring in the spring and fall are the typical patterns of precipitation. In urban streams such as those within the Carters Creek basin storm runoff is channeled directly to receiving water without passing through a WWTP. Stream flow during the dry summers in the region is believed to predominantly be irrigation runoff or effluent from WWTP (Aitkenhead-Peterson et al. 2009; Steele and Aitkenhead-Peterson 2012). The sampling sites were assessed for ease of access and probable flow volume permitting sampling. Stream crossings such as bridges were chosen to facilitate ease of sampling. Samples were collected on the upstream side of the bridge to avoid overwhelming signatures of fecal matter from cliff swallows that are known to commonly reside underneath bridges. All 12 sampling sites were situated along the longitudinal path of the stream. A range of 1^{st}, 2^{nd}, and 3^{rd} order streams were selected to best represent the spatial distribution of source pollutants. The headwaters of Carters Creek basin were sampled, as well as one sample (Carter 5) downstream of the Bryan Waste Water Treatment Facility situated on Burton Creek. The majority of Burton Creek tributary sampling sites were in heavily urbanized areas of Bryan-College Station (Figs 2.2 and 2.3).

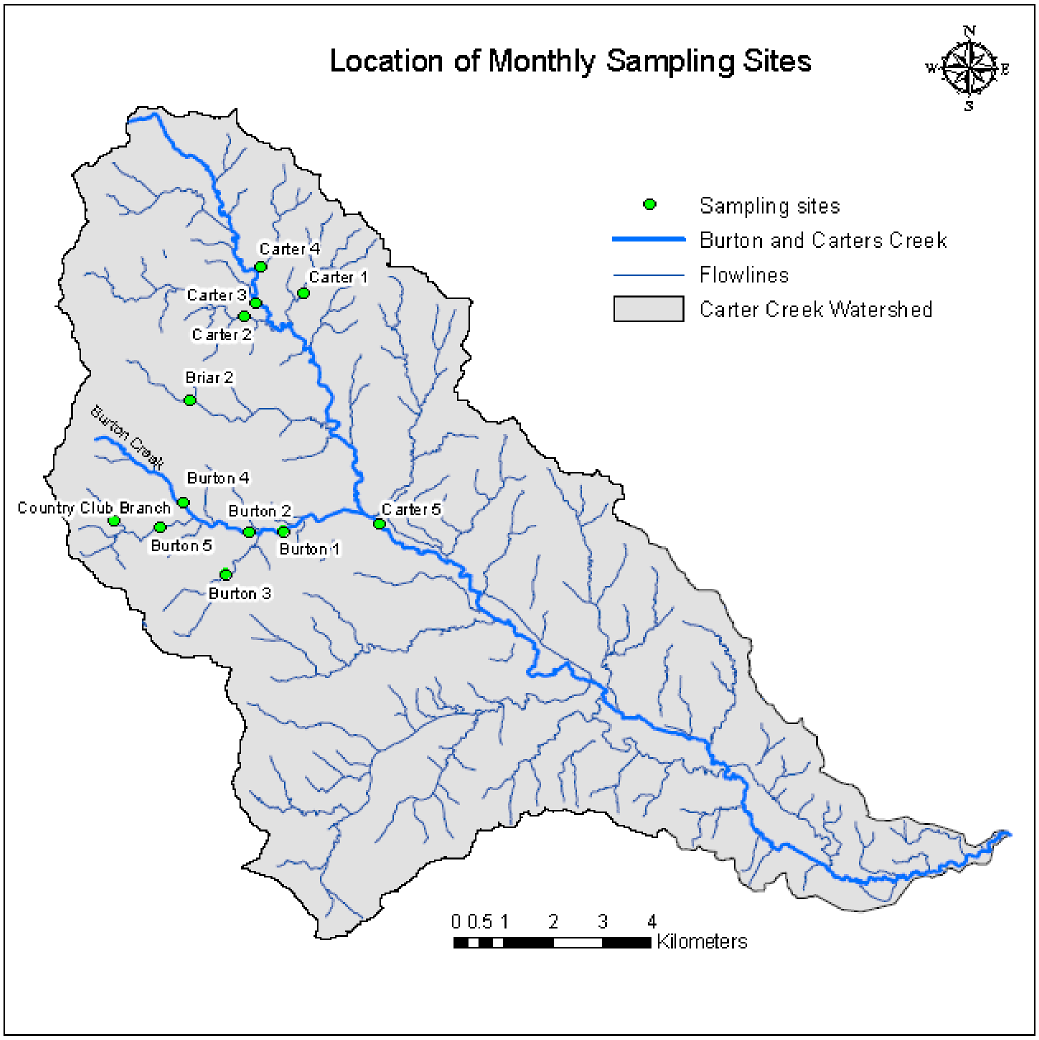


Fig. 2.2 Location of sampling sites in the Carters Creek basin

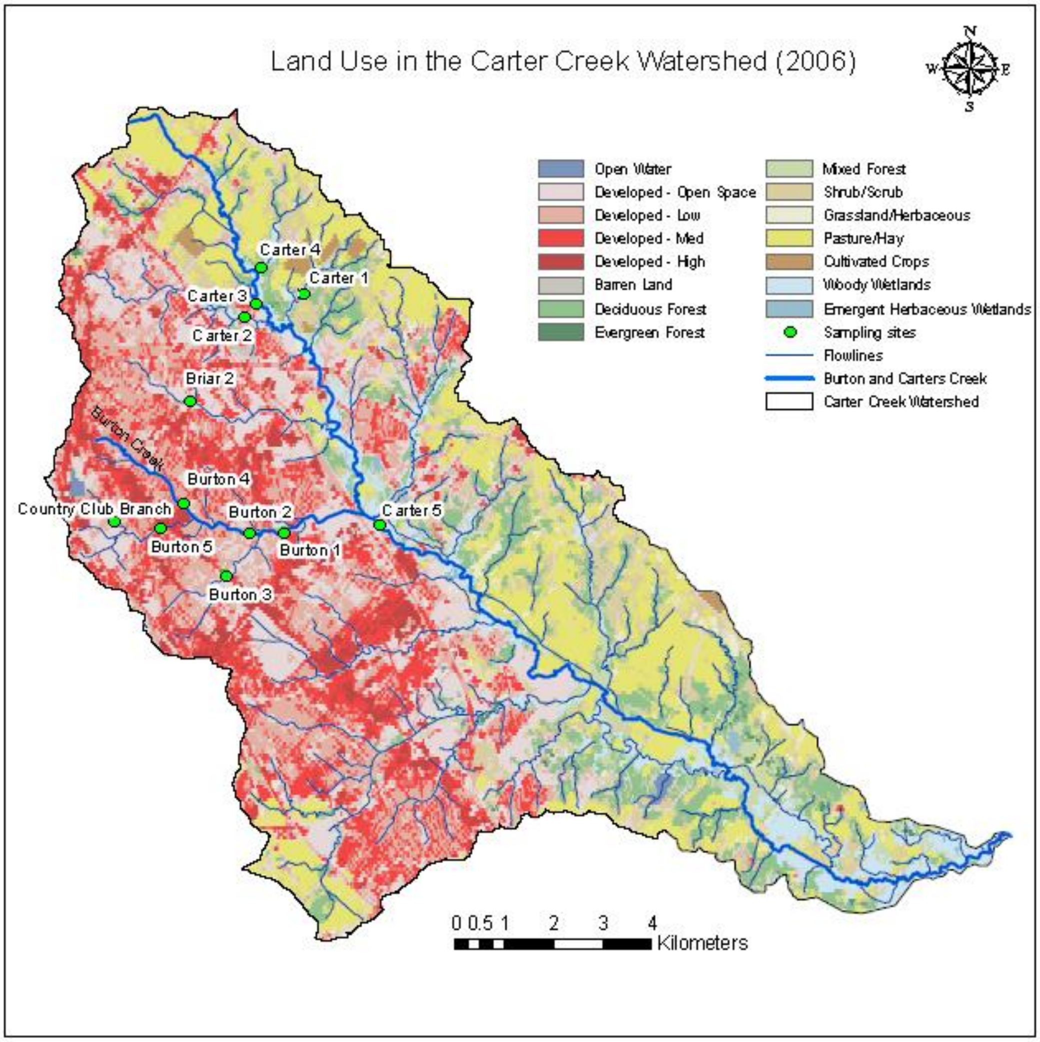


Fig. 2.3 Land use classification (2006) in the Carters Creek basin with sampling sites

Land use in the watersheds was mainly urban in the Burton Creek watersheds (Fig 2.3; Table 2.1) and pasture in the upper Carters Creek 1st order watersheds (Fig 2.3; Table 2.1). Subwatersheds with < 50% urban land use were assigned a rural classification. Urban areas in the region consist of both asphalt and concrete impervious surfaces, on roads, in parking lots and neighborhoods. The type of urban areas in each subwatershed is illustrated in Table 2.2.

Table. 2.1 Percent land use in the study watersheds

	Area	Urban	Agriculture	Range	Shrub	Forest	Wetland	Barren	Open Water
	km^2				%				
Rural									
Carter 1	2.6	0.4	57.1	1.4	21.0	14.4	4.6	0	1.1
Carter 3	11.6	24.8	45.9	1.0	14.3	9.0	4.8	0.2	0
Carter 4	2.3	9.1	39.1	0.8	30	14.0	6.6	0.4	0
Urban									
Carter 5	15.7	69.4	13.9	0.7	5.9	5.3	4.3	0.3	0.2
Carter 2	7.6	85.2	3.8	0.7	5.7	2.3	2.0	0.1	0
Burton 1	10.7	99.0	0	0.1	0	0.1	0	0	0.7
Burton 2	2.4	98.7	0	0.1	0	0.2	0	0	1.0
Burton 3	3.4	99.7	0	0.3	0	0	0	0	0
Burton 4	4.3	100.0	0	0	0	0	0	0	0
Burton 5	2.8	96.7	0.2	0.2	0.1	0.4	0	0	2.5
Briar 2	1.6	100.0	0	0	0	0	0	0	0
CCB	57.3	91.7	0	0.4	0	1.2	0	0	6.8

CCB = Country Club Branch. Rural classification for sites with < 50% urban land use.

Table 2.2 Percent urban land use in the study watersheds

	Open Space	Low	Medium	High	Total Urban
			%		
Carter 1	0.3	0	0.0	0.0	0.4
Carter 2	35.2	27.7	17.8	4.5	85.2
Carter 3	11.0	6.2	6.3	1.3	24.8
Carter 4	7.0	2.1	0	0	9.1
Carter 5	21.2	23.7	19.1	5.4	69.4
Burton 1	20.4	37.7	30.0	10.9	99.0
Burton 2	18.2	37.5	30.7	12.3	98.7
Burton 3	26.1	41.9	25.0	6.7	99.7
Burton 4	10.0	43.7	33.7	12.7	100.0
Burton 5	28.7	29.5	28.5	10.1	96.7
Briar 2	18.4	50.2	27.2	4.1	100.0
CCB	22.9	29.9	28.9	10.0	91.7

CCB = Country Club Branch

2.2.2 Nested Watershed Approach

Watershed subdivision into smaller units known as subwatersheds has been used for hierarchical spatial characterization and examination of water quality (Hunsaker and Levine, 1995) and hydrology (McNamara et al. 1998). Comparisons of stream water chemistry at the subwatershed level with larger subwatersheds can indicate towards problematic areas of elevated nutrient loadings (Hunsaker and Levine, 1995). In this study all future references to nutrients specifically identify C, N and P. Identification of such 'hot-spots' is helpful to watershed planners for directing their limited resources appropriately. In this study subwatershed delineated from sampling sites on tributaries of Burton Creek (Fig 2.2) were compared with larger watershed chemistry in a nested-approach to identify relative nutrient addition and dilution effects along the longitudinal path of Burton Creek

2.2.3 Field Sampling

Stream water samples were collected each month at the 12 sites in Carters Creek basin (Figs 2.2 and 2.3). A study in the watershed in 2007 utilized the nested watershed approach to examine stream nutrients (Harclerode et al. 2013). Many of the nested sites which were monitored in 2007 by Harclerode et al. (2013) were included in this study with some additions of new rural subwatersheds in the northern reaches of the watershed that have become accessible with sub-division development in the basin since 2007.

Stream water was collected using 500 mL sterile whirlpak bags attached to stream sampling apparatus. Samples were transported to the lab within 4 hours of collection. Under extremely low flow conditions, grab samples were collected directly from streams where bank access allowed. In this case samples were collected directly into whirlpak bags from the deepest point in the channel where flow was evident.

2.2.4 Chemical Analysis

Aliquots of stream samples were syringe filtered through ashed (400 °C for 5 h) Whatman GF/F filters (0.7 μm nominal pore size). Samples were either analyzed on the day of collection or frozen in acid-washed high-density polyethylene bottles. DOC and total dissolved nitrogen (TDN) were measured using high temperature Pt-catalyzed combustion with a Shimadzu TOC-VCSH and Shimadzu total measuring unit TNM-1 (Shimadzu Corp. Houston, TX, USA). Dissolved organic carbon was measured as non-purgeable carbon (USEPA method 415.1) which entails acidifying the sample and sparging for 4 min with C-free air. Ammonium-N was analyzed using the phenate hypochlorite method with sodium nitroprusside enhancement (USEPA method 350.1) and nitrate-N was analyzed using Cd-Cu reduction (USEPA method 353.2). Orthophosphate-P was quantified using the ammonium molybdate method. Colorimetric methods were performed with a Smartchem DiscreteAnalyzer (Model 200 Westco Scientific Instruments Inc., Brookfield, CT, USA). Dissolved organic nitrogen (DON) was estimated by deducting NO_3-N plus NH_4-N from TDN.

Check standards and National Institute of Standards and Technology (NIST) traceable standards were run every 12th sample to test for instrument precision and accuracy. The coefficient of variance between replicates was typically less than 2 % for colorimetric analysis and less than 5 % for DOC and TDN.

2.2.5 Statistical Analysis

To support the assumptions of parametric statistics, water quality data was transformed logarithmically in SPSS prior to statistical analysis. The Shapiro-Wilks statistic test was used to verify the assumption of normal distributions.

Stream samples were examined as annual, high flow and low flow based on daily precipitation data. High flow is stream water collected within 2 days of a significant rain event >0.635cm (0.25”). Table 2.3 shows monthly rainfall in College Station from which high and low flow classification were determined. Average and standard deviation of all streams sampled during a) high and low flow and b) hot and cool season were calculated. Hot season was determined as the months April to October and cold season the months November to March. To test the hypothesis that nutrient concentrations would be higher during high flow a Student’s 1-tail, 2-sample t-tests ($\alpha<0.05$) were applied to the data to determine if significant differences exist in the watersheds between the two flow regimes.

Table. 2.3 Monthly rainfall in College Station, TX in the 3 days preceding sampling events. (H) indicates high flow and (L) low flow

	Rainfall (inches)			
	24h	48h	72h	Total
Jul-12 (H)	0	0.06	0.96	1.02
Aug -12 (H)	0.41	0.16	0.84	1.41
Sep-12 (H)	0.36	0	0	0.36
Oct-12 (L)	0	0	0	0
Nov-12 (L)	0	0	0	0
Dec-12 (H)	1.85	0	0	1.85
Jan-13 (L)	0.02	0	0	0.02
Feb-13 (L)	0.13	0.02	0	0.15
Mar-13 (L)	0	0	0	0
Apr-13 (H)	0	0	0.34	0.34
May-13 (H)	1.13	0	0	1.13
Jun-13 (L)	0	0	0	0

Pearson bivariate correlation analysis was used on log transformed stream data and percent watershed land use to determine relationships between nutrient concentrations during a) high flow and b) low flow and watershed land use.

2.3 RESULTS

During 12 months of sampling from July 2012-June 2013, 6 events were classified as low flow events and 6 events as high flow. Annual stream chemistry values across the watershed were as follows. pH ranged from 7.7-9.4 and electrical conductivity from 120-1313 µS cm^{-1}. Nitrate-N concentrations ranged 0.16 to 22.84 mg L^{-1}, ammonium-N from 0.19-1.71 mg L^{-1} and orthophosphate-P from 0.11-3.60 mg L^{-1}. DOC averaged 18.6-57.0 mg L^{-1} and DON ranged 0.47-2.88 mg L^{-1}. Average C, N and P concentrations were higher during high flow. No immediate effect of seasonality was determined in this study.

2.3.1 Carbon, Nitrogen and Phosphorus Concentrations during High and Low Flows

The first hypothesis stated that pH, EC and nutrient concentrations would be significantly higher in streams during high flow because nutrients examined in this study typically have a watershed rather than groundwater source. Mean annual stream water chemistry is presented in Table 2.4. This hypothesis was accepted in part for pH. Briar 2, Burton 1, Burton 4, Burton 5 and Carter 2 had significantly higher pH during high flow compared to low flow (Fig 2.4). For the other streams there was no significant difference in pH when comparing high and low flows (Fig 2.4). pH ranged from 7.4 to 9.3 during low flow and from 7.2 to 8.4 at high flow. Lowest pH was measured at Carter 1 both at low (7.4±0.7) and high flows (7.2±1.0). The highest pH was measured at Burton 2 both at low (9.3±0.8) and at high flow (8.4±1.0).

Table. 2.4 Mean annual values for selected stream parameters for monitoring sites in the study at high and low flows. Values in parentheses are standard deviations

	pH		EC, $\mu S\ cm^{-1}$		NO_3-N, mg L^{-1}		NH_4-N, mg L^{-1}	
	Low	High	Low	High	Low	High	Low	High
Briar 2	8.04 (0.36)	7.70 (0.11)	434 (63)	306 (147)	0.40 (0.45)	0.28 (0.13)	0.24 (0.02)	0.26 (0.05)
Burton 1	8.75 (0.35)	7.83 (0.68)	737 (188)	431 (299)	0.70 (0.35)	0.29 (0.23)	0.22 (0.02)	0.24 (0.04)
Burton 2	9.28 (0.42)	8.42 (1.00)	1153 (388)	462 (243)	0.12 (0.05)	0.22 (0.10)	0.20 (0.02)	0.23 (0.05)
Burton 3	8.25 (0.18)	8.04 (0.31)	1078 (171)	534 (190)	0.15 (0.09)	0.21 (0.07)	0.21 (0.02)	0.22 (0.03)
Burton 4	8.88 (0.75)	8.01 (0.60)	907 (550)	340 (122)	0.12 (0.05)	0.27 (0.13)	0.21 (0.01)	0.26 (0.08)
Burton 5	8.31 (0.16)	7.95 (0.11)	854 (199)	485 (246)	0.16 (0.06)	0.82 (1.30)	0.20 (0.02)	0.29 (0.07)
Carter 1	7.40 (0.74)	7.20 (1.01)	256 (56)	120 (44)	0.28 (0.17)	0.47 (0.37)	0.22 (0.03)	0.31 (0.06)
Carter 2	8.23 (0.40)	7.67 (0.34)	484 (68)	323 (115)	0.14 (0.05)	0.30 (0.16)	0.20 (0.01)	0.25 (0.05)
Carter 3	8.37 (0.08)	7.91 (0.41)	333 (35)	282 (93)	0.16 (0.03)	0.20 (0.10)	0.21 (0.01)	0.24 (0.04)
Carter 4	8.05 (0.61)	7.81 (0.61)	891 (293)	550 (283)	0.67 (1.05)	0.40 (0.49)	0.27 (0.05)	0.23 (0.03)
Carter 5	8.21 (0.11)	8.02 (0.29)	1313 (117)	761 (430)	22.84 (2.61)	9.64 (9.18)	0.23 (0.02)	0.28 (0.12)
CCB	8.00 (0.13)	7.85 (0.18)	585 (249)	456 (173)	0.13 (0.08)	0.19 (0.10)	0.19 (0.02)	1.71 (3.29)

Table. 2.4 Continued

	PO_4-P, mg L^{-1}		DOC, mg L^{-1}		DON, mg L^{-1}	
	Low	High	Low	High	Low	High
Briar 2	0.23 (0.06)	0.30 (0.17)	35.5 (11.8)	36.3 (13.5)	0.51 (0.14)	0.94 (0.56)
Burton 1	0.21 (0.04)	0.23 (0.11)	49.7 (14.7)	43.1 (28.3)	0.64 (0.28)	1.03 (0.98)
Burton 2	1.29 (2.40)	0.19 (0.10)	50.9 (30.7)	51.7 (30.2)	1.09 (0.34)	1.58 (1.05)
Burton 3	0.14 (0.06)	0.28 (0.16)	50.1 (29.8)	41.0 (20.2)	0.47 (0.25)	0.93 (0.80)
Burton 4	0.20 (0.12)	0.31 (0.15)	68.1 (66.0)	37.4 (18.2)	1.19 (0.88)	1.30 (0.59)
Burton 5	0.17 (0.08)	0.36 (0.22)	43.6 (16.3)	40.5 (22.1)	0.91 (0.62)	1.40 (1.13)
Carter 1	0.10 (0.07)	0.24 (0.13)	35.4 (11.5)	18.6 (5.1)	1.04 (0.38)	0.84 (0.54)
Carter 2	0.14 (0.09)	0.18 (0.06)	41.7 (22.5)	38.8 (16.5)	0.75 (0.27)	0.94 (0.49)
Carter 3	0.11 (0.05)	0.22 (0.12)	23.1 (13.9)	33.3 (15.2)	0.47 (0.22)	1.02 (0.59)
Carter 4	0.16 (0.25)	0.11 (0.06)	49.4 (19.5)	35.5 (24.2)	0.73 (0.70)	0.78 (0.40)
Carter 5	3.60 (0.28)	1.80 (1.44)	57.0 (34.0)	51.6 (23.1)	2.88 (5.45)	1.99 (2.65)
CCB	0.22 (0.09)	0.43 (0.47)	37.2 (31.5)	54.0 (27.8)	0.69 (0.20)	1.72 (1.70)

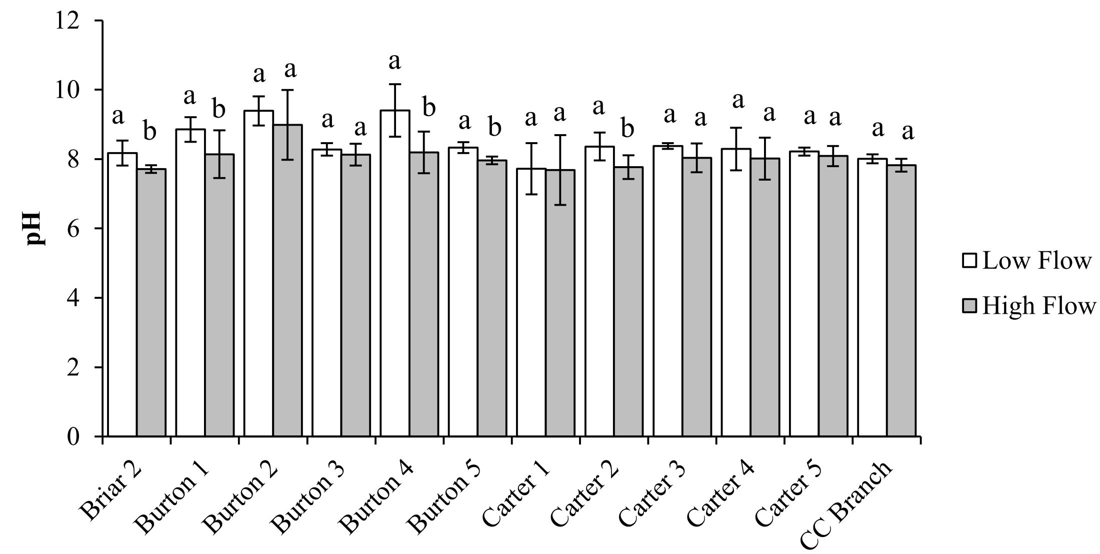


Fig. 2.4 pH of streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For each individual stream, difference in lower case letter indicates a significant difference between high and low flow at α = 0.05

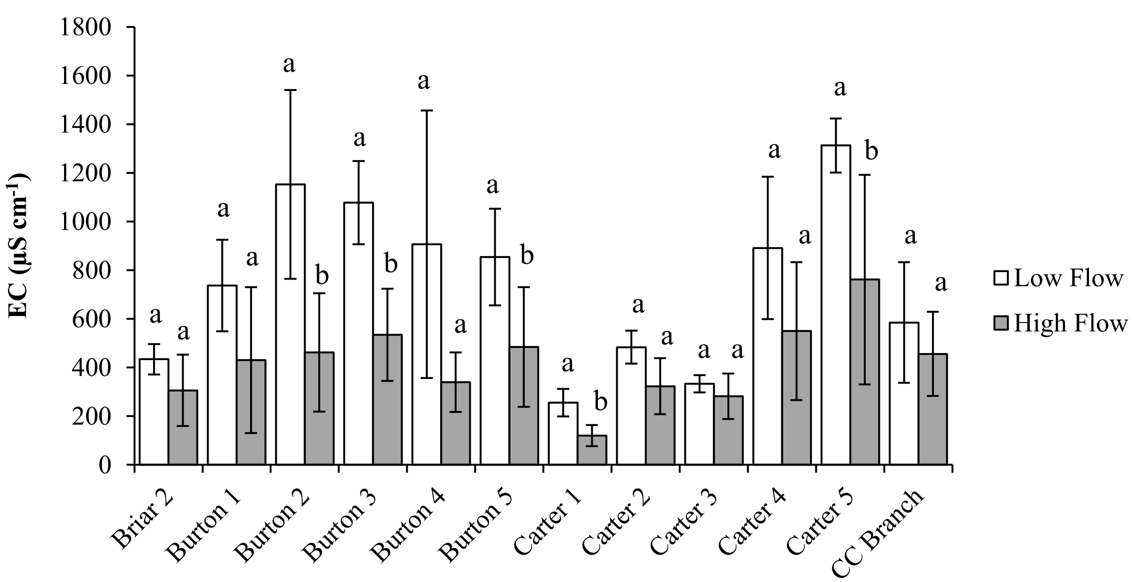


Fig. 2.5 Electrical conductivity of streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For each individual stream, difference in lower case letter indicates a significant difference between high and low flow at α = 0.05

Higher EC was observed in all streams under low flow conditions (Fig 2.5). This difference was statistically significant in Burton 2, Burton 3, Burton 5, Carter 1 and Carter 5. No significant difference was found in the other streams when comparing high and low flows. The lowest average conductivity was 256±63 μS cm^{-1} during low flow and 120±44 μS cm^{-1} at high flow, both at Carter 1. Highest EC was measured at Carter 5, 1313±112 μS cm^{-1} under low flow, and 761±430 μS cm^{-1} under high flow.

Rural headwater streams such as Carter 1 and Carter 3 displayed lower standard deviations in comparison to their urban counterparts such as Country Club Branch, Burton 2 and Burton 3. On average, Burton creek sites had higher conductivity than Carter sites with the exception of Carter 5. These results contradict my hypothesis of higher conductivity observed for high flow.

Nitrate-N concentrations were below the permitted EPA drinking water quality standard of 10 mg L^{-1} at all sites except Carter 5. There were some significant differences in nitrate-N concentration between low and high flow. Significantly higher concentrations were found at Burton 3, Burton 4, Burton 5and Carter 2 at high flow, and Carter 5 at low flow (Fig 2.6). All the other streams showed no significant difference between flow conditions. Carter 5 had significantly higher nitrate-N concentrations compared to all the other streams.

Nitrate-N ranged from 0.12±0.05 mg L^{-1} at low flow at Burton 4 to 0.20±0.10 mg L^{-1} at high flow at Carter 2. Highest concentrations were measured at Carter 5 both for low and high flow. They ranged from 23±2.6 mg L^{-1} at low flow to 9.6±9.2 mg L^{-1} at high flow.

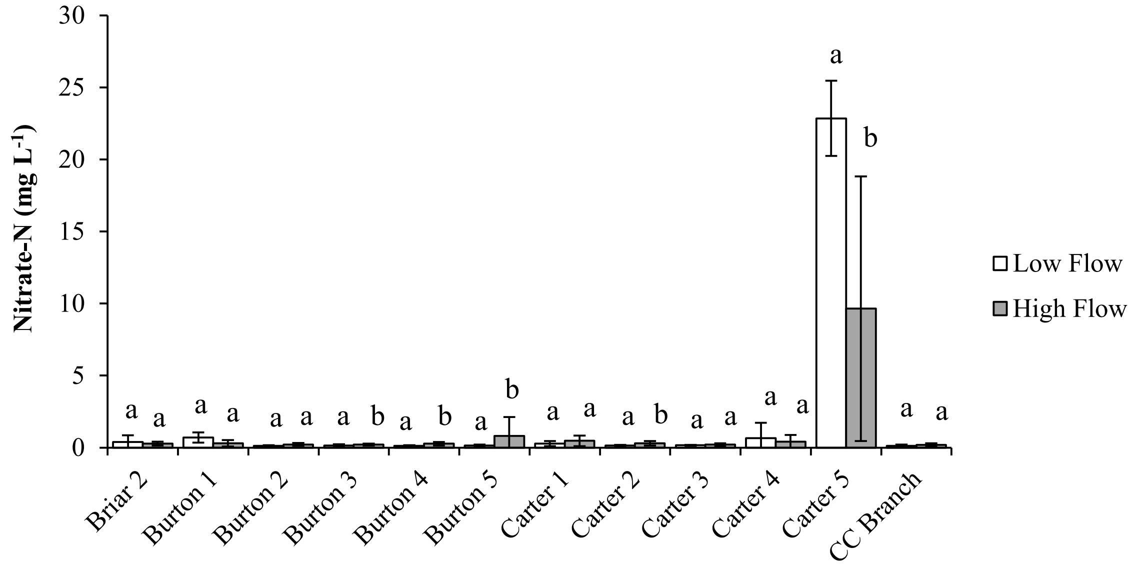


Fig. 2.6 Nitrate-N in streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For each individual stream, difference in lower case letter indicates a significant difference between high and low flow at $\alpha = 0.05$

Ammonium-N concentrations were relatively similar regardless of flow conditions (Fig 2.7). Despite significant differences at three sites, the range of ammonium-N concentration was remarkably small. Standard deviations ranged from 0.01-0.05 mg L^{-1} at low flow to 0.03-3.29 mg L^{-1} at high flow. The lowest average ammonium-N concentration was 0.19±0.02 mg L^{-1} during low flow at Country Club Branch and 0.22±0.03 mg L^{-1} at high flow at Burton 3. Highest concentrations were measured at Carter 4 0.27±0.05 mg L^{-1} under low flow, and 1.71±3.29 mg L^{-1} at Country Club Branch under high flow.

Significant differences in ammonium-N concentrations between high and low flows were found at Burton 5, Carter 1, and Carter 2 where ammonium-N concentrations were higher at high relative to low flow (Fig 2.7). All the other streams showed no significant difference between flow conditions. Country Club Branch had exceptionally higher ammonium-N concentrations during high flow when compared to the other streams but the amount of variance was also high (Fig 2.7).

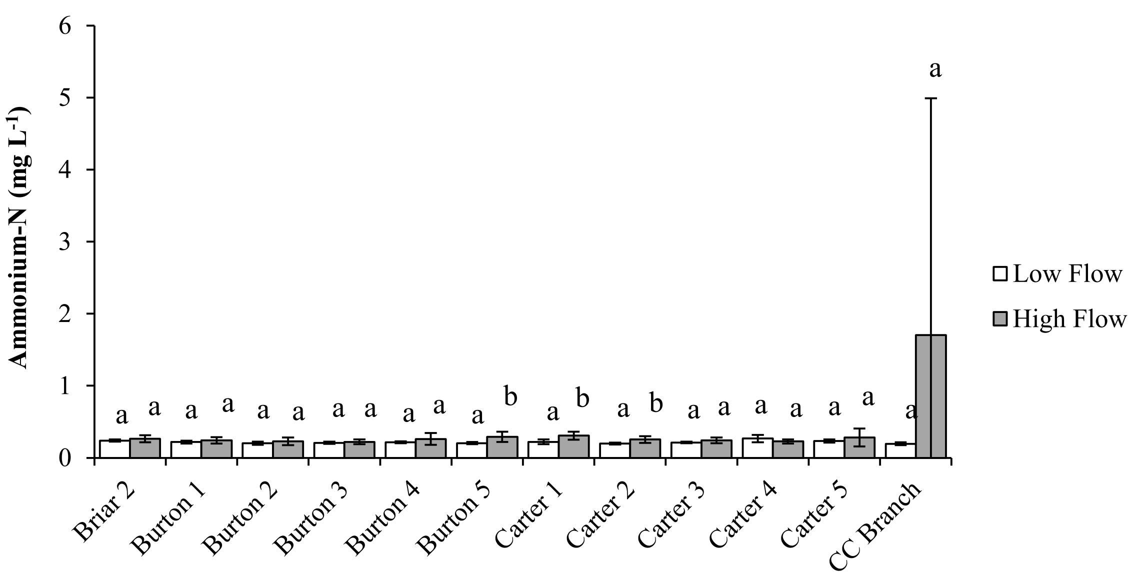


Fig. 2.7 Ammonium-N in streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For each individual stream, difference in lower case letter indicates a significant difference between high and low flow at $\alpha = 0.05$

Significant differences between high and low flow were found only at Carter 1 where DOC concentration was significantly higher during low flow (Fig 2.8). DOC concentrations were higher at all streams during low flow except at Briar 2, Burton 2, Carter 3 and Country Club Branch (Fig 2.8).

The lowest average DOC concentration was 23.1±13.8 mg L^{-1} during low flow at Country Club Branch and 18.6±5.1 mg L^{-1} at high flow at Carter 1. Highest concentrations were measured at Burton 4, 68.1±66.0 mg L^{-1} under low flow, and 54.0±27.8 mg L^{-1} at Country Club Branch under high flow.

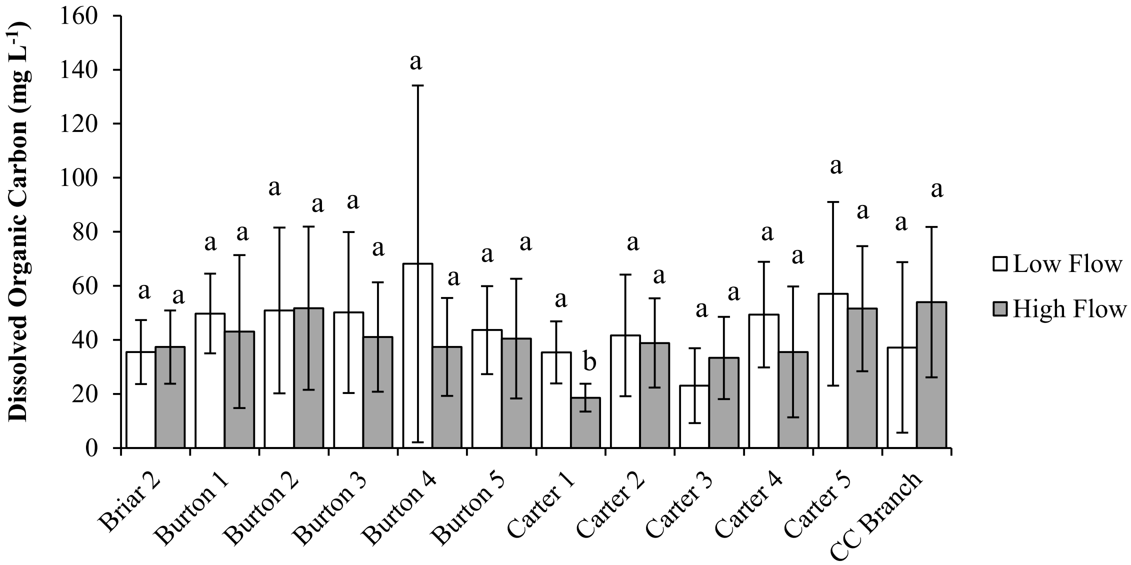


Fig. 2.8 Dissolved organic carbon (DOC) in streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For individual streams, difference in lower case letter indicates a significant difference between high and low flow at $\alpha = 0.05$

No significant differences between high and low flow were found for DON concentrations (Fig 2.9). Lowest average DON concentration was 0.47±0.22 mg L^{-1} during low flow at Carter 3 and 0.78±0.40 mg L^{-1} during high flow at Carter 4. Highest concentrations were measured at Carter 5 both under high and low flow (2.88±5.4 mg L^{-1} at low flow and 1.99±2.65 mg L^{-1} at high flow). The range of DON concentrations at Carter 5 was greater than all other sites (Fig 2.9).

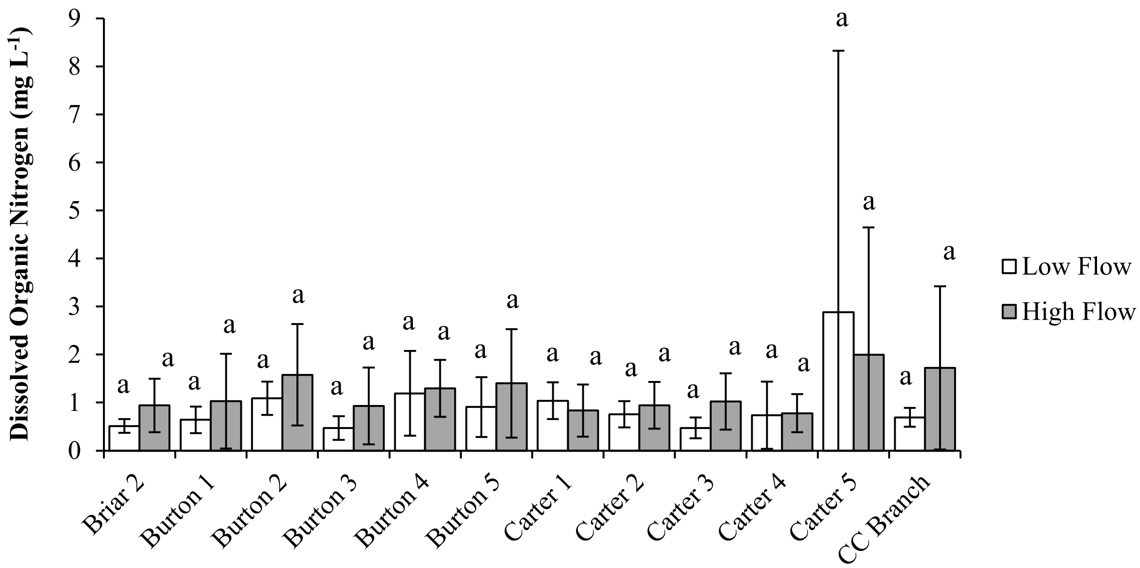


Fig. 2.9 Dissolved organic nitrogen (DON) in streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For each individual stream, difference in lower case letter indicates a significant difference between high and low flow at $\alpha = 0.05$

Significant differences between high and low flow for orthophosphate-P were found at Burton 3, Burton 5, Carter 1, Carter 3, and Carter 5 (Fig 2.10). Orthophosphate-P concentrations tended to be higher during high flow conditions relative to low flow conditions (Fig 2.10). The other streams showed no significant difference between flow conditions. Nine of the twelve streams had higher orthophosphate levels during high flow however Burton 2, Carter 4 and Carter 5 had higher orthophosphate-P during low flow.

The lowest average orthophosphate-P was 0.11±0.05 mg L^{-1} during low flow at Carter 3 and 0.11±0.06 mg L^{-1} at high flow at Carter 4. Highest concentrations were measured at Carter 5, 3.60±0.30 mg L^{-1} under low flow, and 1.80±1.44 mg L^{-1} at under high flow.

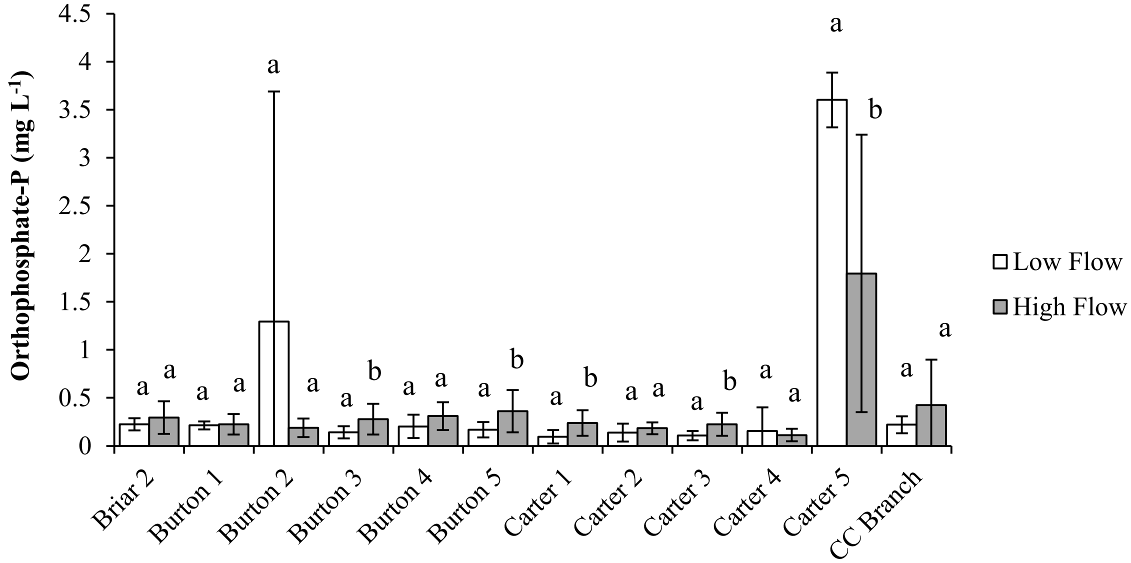


Fig. 2.10 Orthophosphate-P in streams in the Carters Creek basin during low flow and high flow. Error bars are standard deviation. For each individual stream, difference in lower case letter indicates a significant difference between high and low flow at α = 0.05

2.3.2 Correlations Between Watershed Land Use and Stream Nutrient Concentrations

Water quality was more strongly correlated with land use during high flow as opposed to low flow (Table 2.5). DOC concentrations were significantly and positively correlated to urban land use during high flow and significantly and negatively correlated with agriculture, rangeland, forest, and wetlands under high flow (Table 2.5). No significant correlations were found between DOC concentrations and land use at low flow (Table 2.5).

Orthophosphate-P showed significant negative correlations with a few land uses; range, wetland, and barren land use, at high flow. At low flow, positive correlations with range and barren were still significant, however not with wetland (Table 2.5). No other parameters displayed significant correlations with any land use.

Table. 2.5 Correlations (R) of water quality parameters with land use at high and low flow

	pH	EC	NO_3-N	NH_4-N	PO_4-P	DOC	DON	DOC/DON
HIGH FLOW								
Urban	ns	ns	ns	ns	ns	0.71*	ns	ns
Agriculture	ns	ns	ns	ns	ns	-0.76**	ns	ns
Range	ns	ns	ns	ns	-0.61*	-0.64*	ns	ns
Forest	ns	ns	ns	ns	ns	-0.71*	ns	ns
Wetland	ns	ns	ns	ns	-0.63*	-0.63*	ns	ns
Barren	ns	ns	ns	ns	-0.65*	ns	ns	ns
LOW FLOW								
	pH	EC	NO_3-N	NH_4-N	PO_4-P	DOC	DON	DOC/DON
Urban	ns	ns	ns	ns	ns	ns	ns	ns
Agriculture	ns	ns	ns	ns	ns	ns	ns	ns
Range	ns	ns	ns	ns	0.64*	ns	ns	ns
Forest	ns	ns	ns	ns	ns	ns	ns	ns
Wetland	ns	ns	ns	ns	ns	ns	ns	ns
Barren	ns	ns	ns	ns	0.63*	ns	ns	ns

* Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed). ns = not significant.

2.3.3 Effect of Climate on Stream Nutrient Concentrations

South-central Texas tends to be either hot or relatively cool so instead of examining seasonal differences in stream nutrient concentrations cool and hot periods were examined separately. To test the effect of climate on water quality, 2-sample, 1-tailed t-tests were run between hot (April-October) and cold (November-March) months (Table 2.6). My hypothesis stated nutrient concentrations during the warm season would be lower than in the colder months due to increased aquatic biological uptake in the creek.

Table. 2.6 Effect of seasonality on water quality (1-tailed, t-test). For individual streams, values in bold and italics indicate a significant difference ($\alpha = 0.05$)

	pH	EC $\mu S\ cm^{-1}$	NO_3-N	NH_4-N	PO_4-P mg L^{-1}	DOC	DON
Briar2	0.23	0.31	0.45	0.18	0.46	0.059	***0.010****
Burton 1	0.29	0.05	0.09	0.30	0.17	0.166	0.239
Burton 2	0.42	0.14	0.42	0.48	0.38	0.495	0.379
Burton 3	0.46	0.15	0.32	0.47	0.28	0.088	0.438
Burton 4	0.36	0.33	0.44	0.42	0.14	0.102	0.482
Burton 5	0.11	0.15	0.33	0.14	0.25	0.383	0.173
Carter 1	0.07	0.44	0.30	0.19	0.13	0.300	0.155
Carter 2	0.12	0.25	0.19	0.36	0.05	0.343	0.496
Carter 3	0.43	0.28	0.36	0.36	0.46	0.381	0.269
Carter 4	0.24	0.48	0.46	0.38	0.10	0.129	0.216
Carter 5	0.48	0.11	0.07	0.10	***0.00****	0.317	0.106
CCB	0.39	0.32	0.40	0.33	0.348	0.339	0.285

* Difference is significant at the 0.05 level (1-tailed).

Climate only had a significant effect for Carter 5 (PO_4-P, $p = 0.003$) and Briar 2 (DON, $p = 0.010$) (Table 2.6). As hypothesized, orthophosphate concentrations in Carter 5 were higher in the warm season than the colder months. Despite lack of significant differences between hot and cold months, patterns in water quality were observed (Fig 2.11- 2.17). Standard deviation was plotted only in the positive direction for legibility.

No significant seasonal differences in pH (Fig 2.11), EC (Fig 2.12), nitrate-N (Fig 2.13) or ammonium-N (Fig 2.14) were found for any creek.

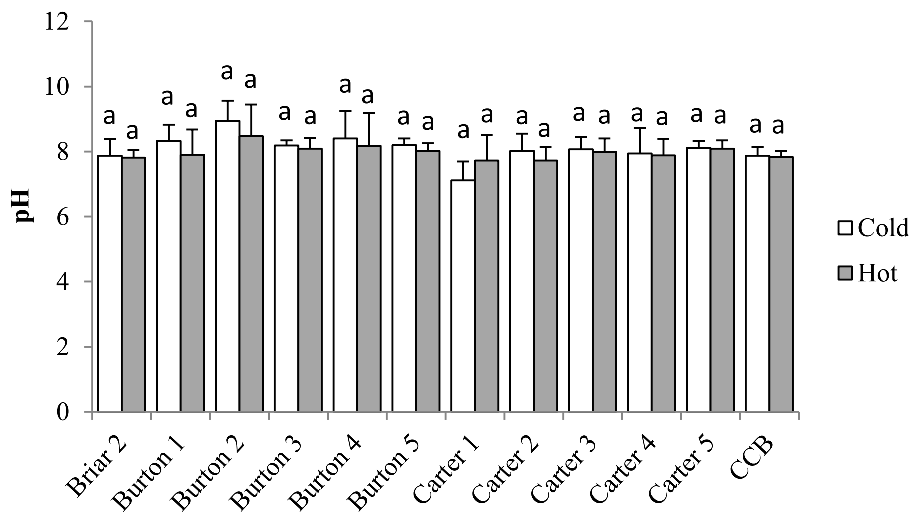


Fig. 2.11 pH in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation.

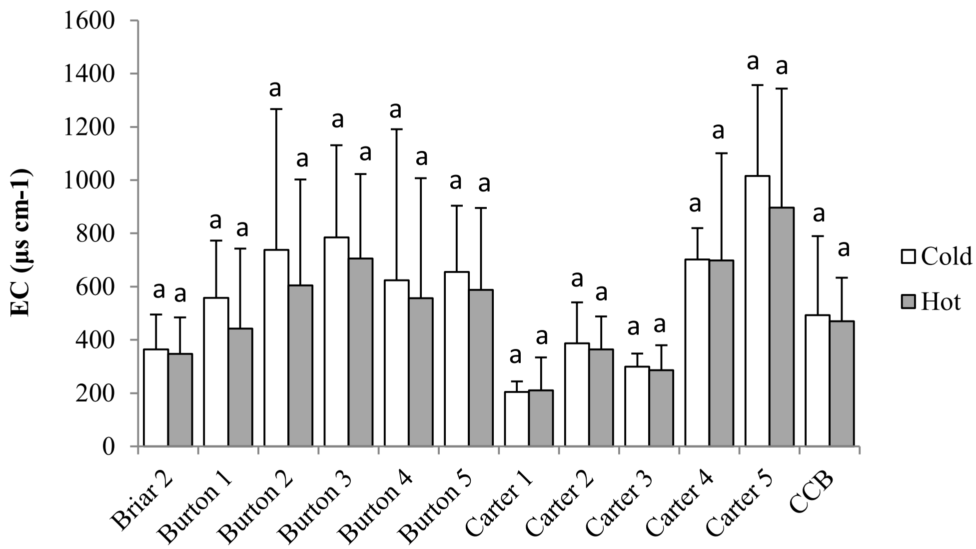


Fig. 2.12 Conductivity in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation.

Nitrate-N concentrations were also higher during the colder months than the warmer months for all streams (Fig 2.13). This result supports my hypothesis that nitrate-N concentration would be lower in the warmer months. This may also result from urban nutrient fertilizer application which occurs in February - May in the study area. The early part of this period, the months of February and March, were included in cold season calculations for the purpose of this study.

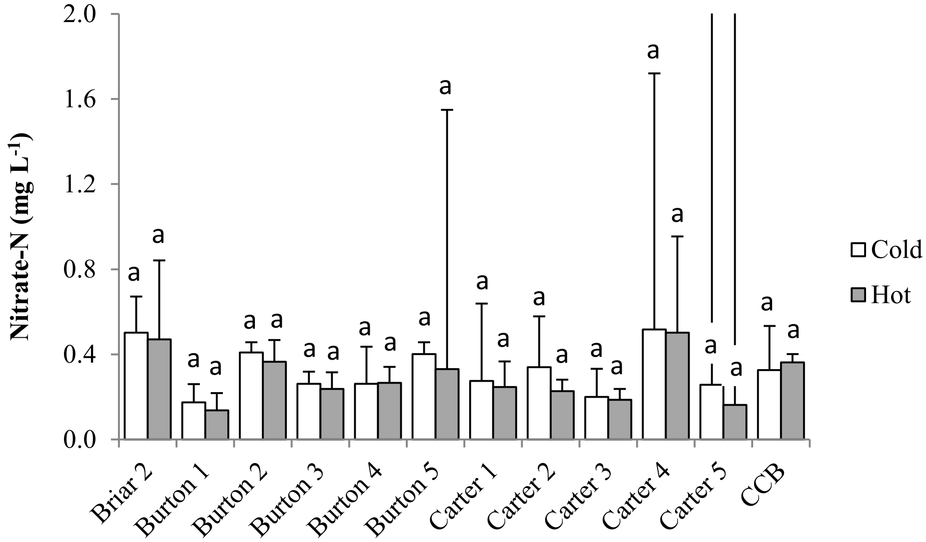


Fig. 2.13 Nitrate-N concentrations in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation. Carter 5 s.d (cold) = 9.4 (hot) = 9.5

No distinct pattern was noticeable in ammonium-N between hot and cold months (Fig 2.14). At some locations such as Briar 2, Burton 5, Burton 1 and Carter 5, higher concentrations were observed during colder months. The opposite was true for all other streams.

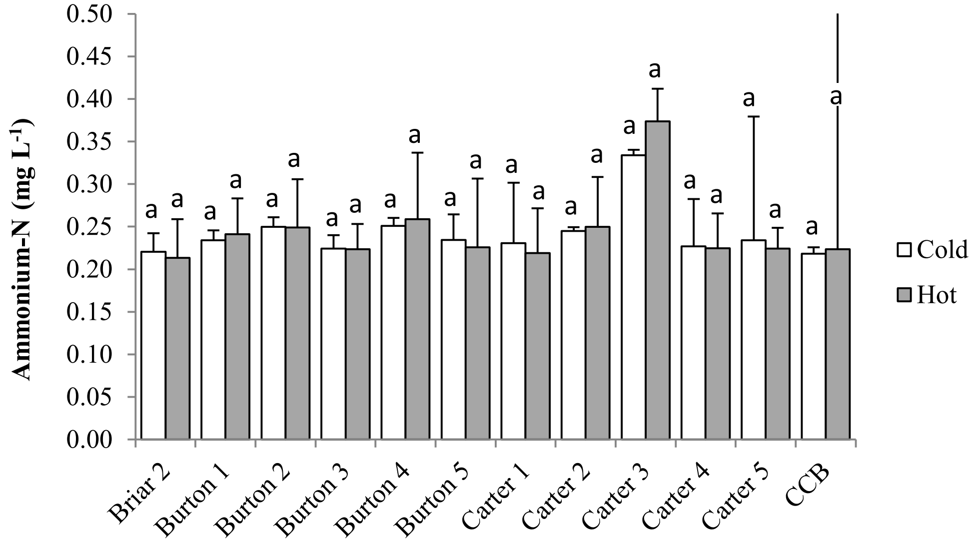


Fig. 2.14 Ammonium-N in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation. CCB standard deviation (hot) = 3.3 mg L^{-1}

Orthophosphate-P was elevated for the majority of streams during colder months. Burton 1-3 showed higher concentrations in warmer months (Fig 2.15). The only statistically significant difference in orthophosphate-P concentration was at Carter 5.

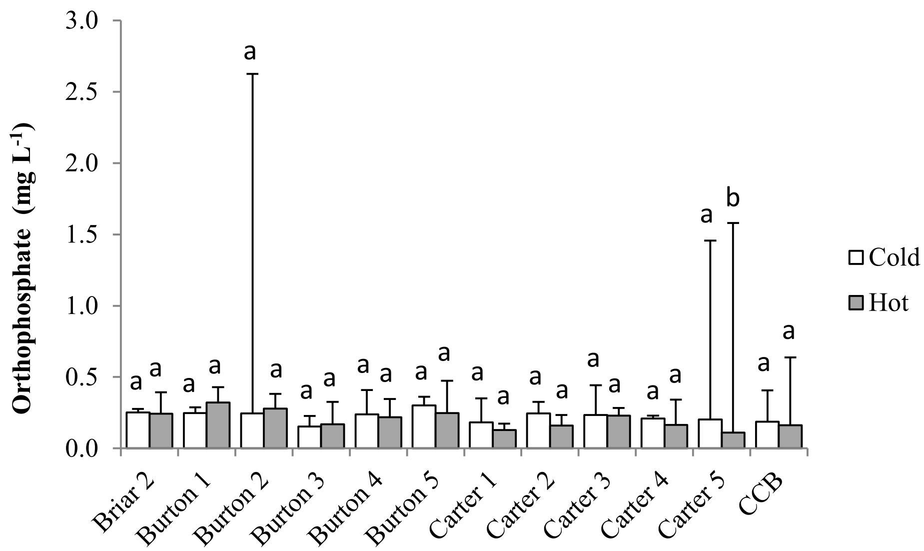


Fig. 2.15 Orthophosphate-P in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation.

No discernible pattern was found in DOC between hot and cold months (Fig 2.16). Higher DOC concentrations were found at Briar 2, Burton 1, Burton 3, Carter 4, and Carter 5 during the warmer months. DOC concentrations were higher during colder months for all other streams. None of the differences observed were significant. Highest DOC concentrations were found at Carter 3. It was predicted that the urban Burton sites would have higher DOC concentrations than their rural counterparts; however patterns in seasonality do not support this hypothesis.

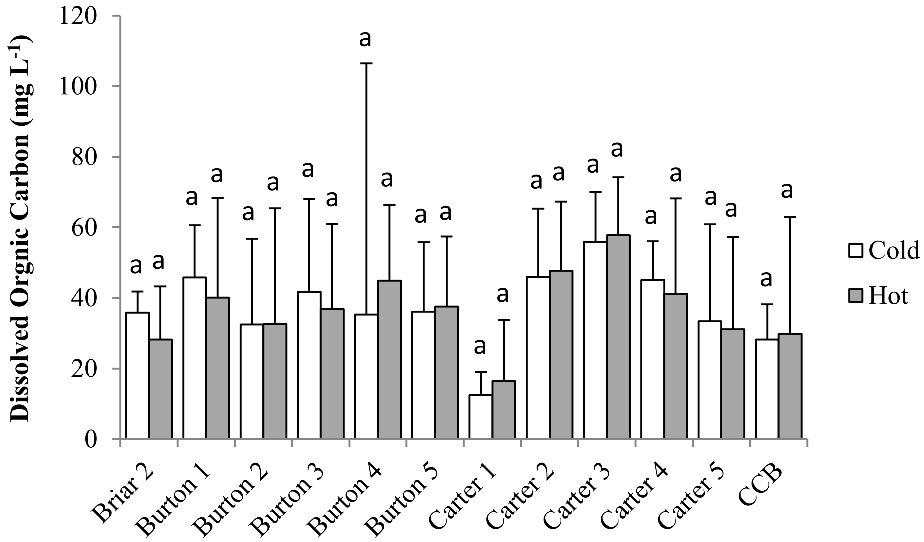


Fig. 2.16 Dissolved organic carbon in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation.

DON was generally higher in the colder months at most streams (Fig 2.17). Burton 2, Burton 3, Burton 5 and Carter 1 showed higher DON concentrations during the hot months. Only Briar 2 displayed a significant difference in DON concentration.

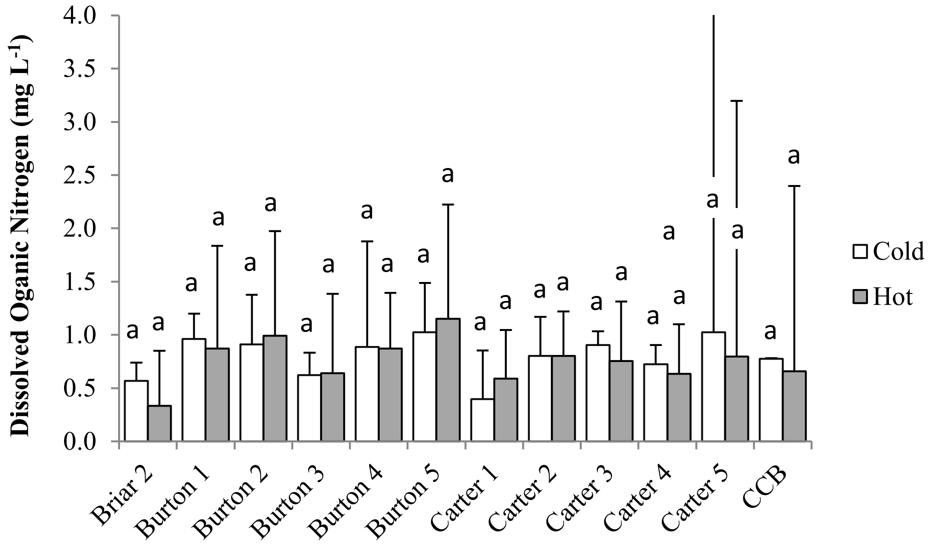


Fig. 2.17 Dissolved organic nitrogen in streams in the Carters Creek basin during hot and cold months. For each individual stream, difference in lower case letter indicates a significant difference between seasons. Error bars are standard deviation. Carter 5 standard deviation (cold) = 6.1

2.3.4 Effects of Addition and Dilution on Water Quality

To test the effects of upstream sites on downstream water chemistry, two-tailed t-tests were run between sites directly upstream/downstream of each other. Only the Burton Creek sites could be assessed due to its nested nature. Significant differences of means between upstream and downstream sites were more prominent at low flow than high flow (Table 2.7).

Table. 2.7 Comparison of stream chemistry at high and low flow to determine addition or dilution effect on downstream sites. (a) indicates an addition effect, (d) indicates a dilution effect

		LOW FLOW						
Upstream	Downstream	pH	EC	NO_3-N	NH_4-N	PO_4-P	DOC	DON
CCB	Burton 5	0.04*(a)	0.02*(a)	ns	ns	ns	ns	ns
Burton 5	Burton 2	0.00**(a)	ns	ns	ns	ns	ns	ns
Burton 4	Burton 2	ns	ns	ns	ns	ns	ns	ns
Burton 3	Burton 1	0.01**(a)	0.00*(d)	0.01**(a)	ns	ns	ns	ns
Burton 2	Burton 1	ns	ns	ns	ns	ns	ns	ns
Burton 1	Carter 5	0.00**(a)	0.00**(a)	0.00**(a)	ns	0.00**(a)	ns	ns
		HIGH FLOW						
Upstream	Downstream	pH	EC	NO_3-N	NH_4-N	PO_4-P	DOC	DON
CCB	Burton 5	ns	ns	ns	ns	ns	ns	ns
Burton 5	Burton 2	0.02*(a)	ns	ns	ns	0.05*(d)	ns	ns
Burton 4	Burton 2	ns	ns	ns	ns	ns	ns	ns
Burton 3	Burton 1	ns	ns	ns	ns	ns	ns	ns
Burton 2	Burton 1	ns	ns	ns	ns	ns	ns	ns
Burton 1	Carter 5	ns	ns	0.00**(a)	ns	0.00**(a)	ns	ns

CCB = Country Club Branch.
*Difference is significant at $\alpha = 0.05$ (two-tailed) ** Difference is significant at $\alpha = 0.01$ (two-tailed). ns = not significant

At low flow, all upstream sites with significant differences downstream contributed an addition effect to downstream locations (Table 2.7). Pairwise site comparisons demonstrated that Burton 4 and 2, and Burton 2 and 1 were the only pairs without any differences between any parameter at low flow. Burton 1 and Carter 5 had significant differences in pH, EC, nitrate-N, and orthophosphate-P (Table 2.7; Figs 2.18-2.21) where Carter 5 displayed an additive effect on stream chemistry. Burton 1 displayed an additive effect relative to Burton 3 at low flow for pH (Table 2.7; Fig 2.18), conductivity (Table 2.7; Fig 2.19), and nitrate-N (Table 2.7; Fig 2.20). Conductivity was the only parameter at Burton 1 relative to Burton 3 with a dilution effect at low flow. Country Club Branch and Burton 5 showed differences between pH and EC with higher values measured at Burton 5 (Figs 2.18 and 2.19). Burton 5 relative to Burton 2 only displayed a difference in pH, also with higher values measured at downstream at Burton 2 (Table 2.7).

At high flow Burton 5 relative to Burton 2 had significantly higher pH (Fig 2.22) and significantly lower orthophosphate-P concentration (Fig 2.24). Burton 1 and Carter 5 showed significant differences with additive effects observed at Carter 5 in nitrate-N (Fig 2.23) and orthophosphate-P (Fig 2.24) concentrations. No other stream combinations had statistically significant addition or dilution effect to downstream sites at low flow.

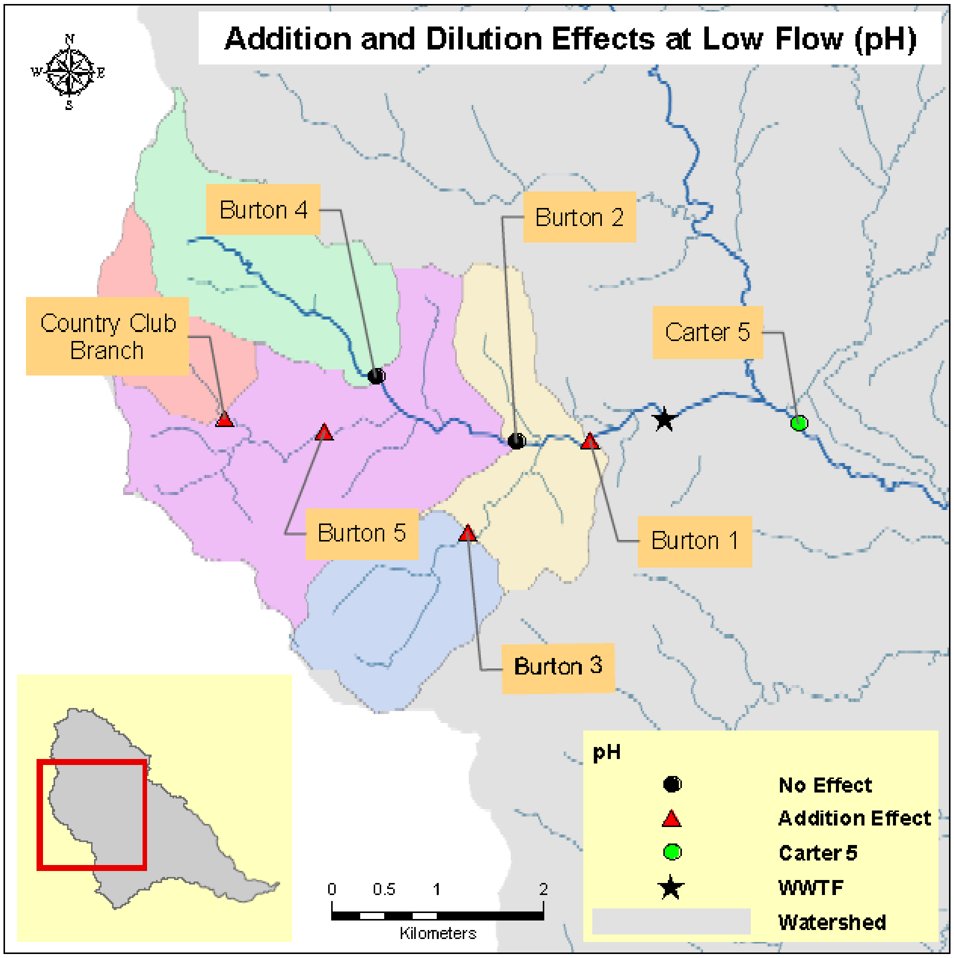


Fig. 2.18 Addition and dilution effects on downstream water quality at low flow (pH)

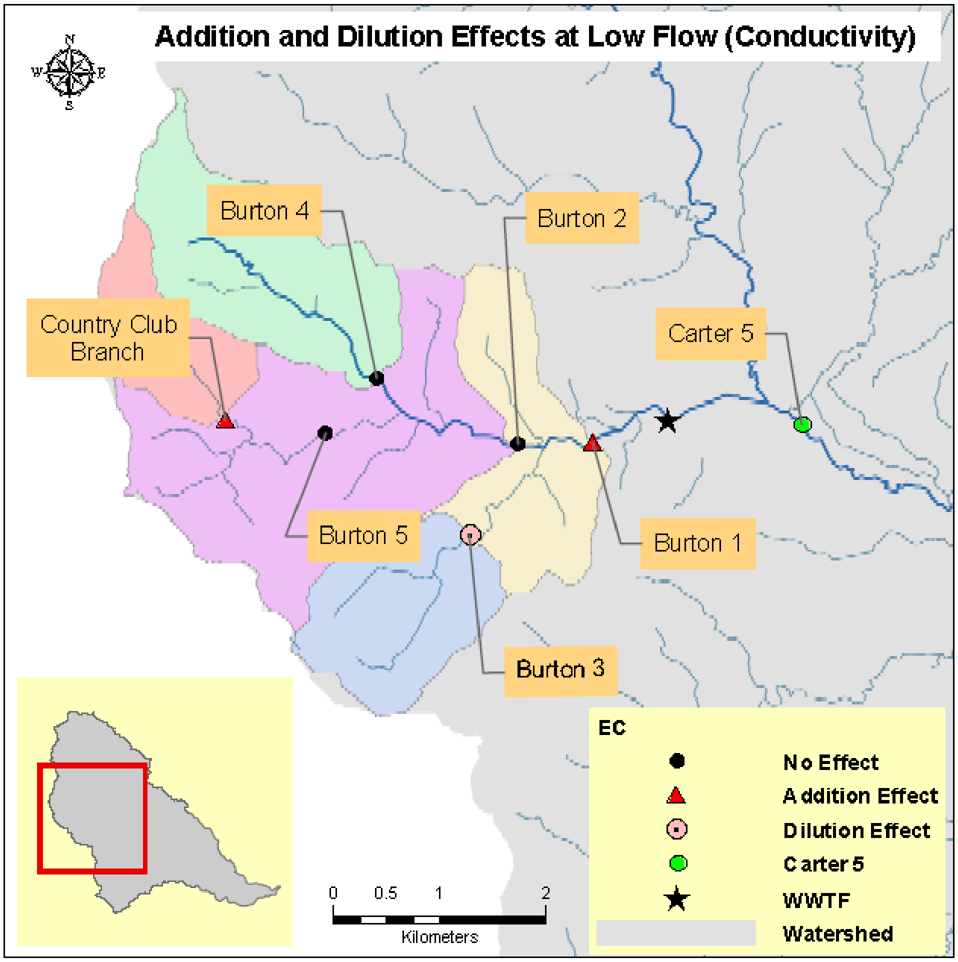


Fig. 2.19 Addition and dilution effects on downstream water quality at low flow (conductivity)

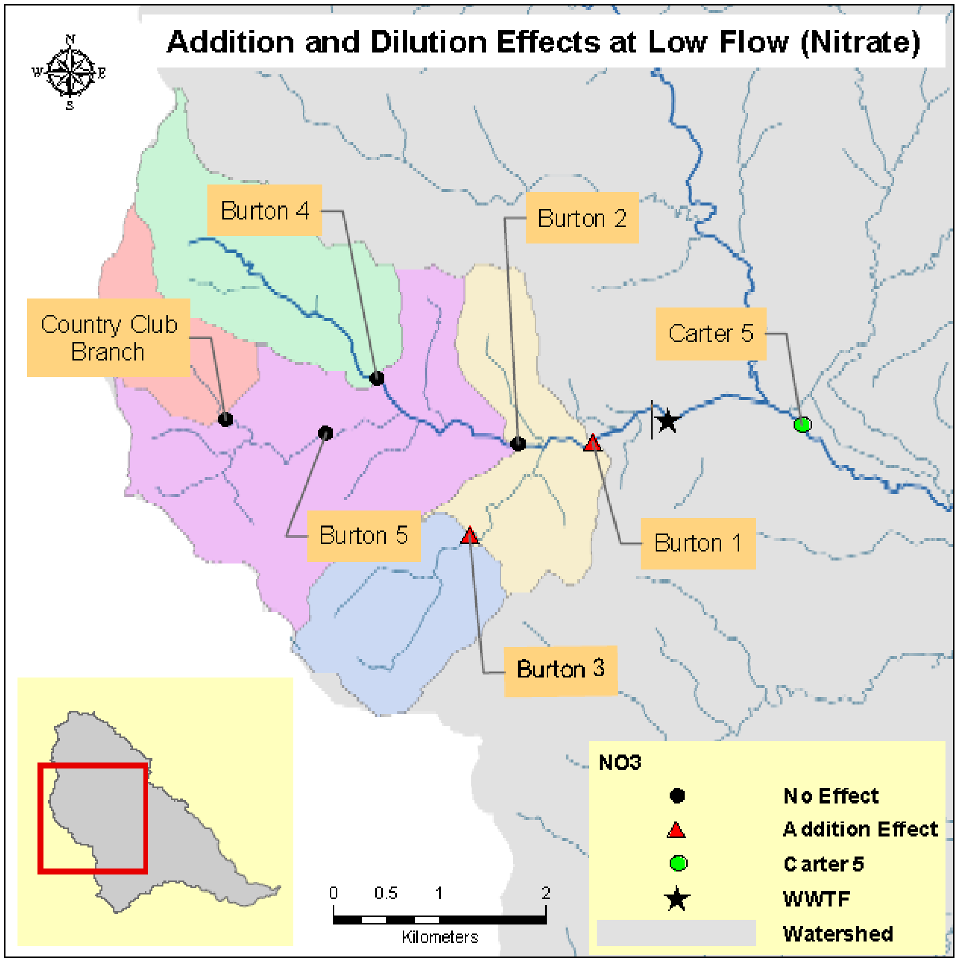


Fig. 2.20 Addition and dilution effects on downstream water quality at low flow (nitrate-N)

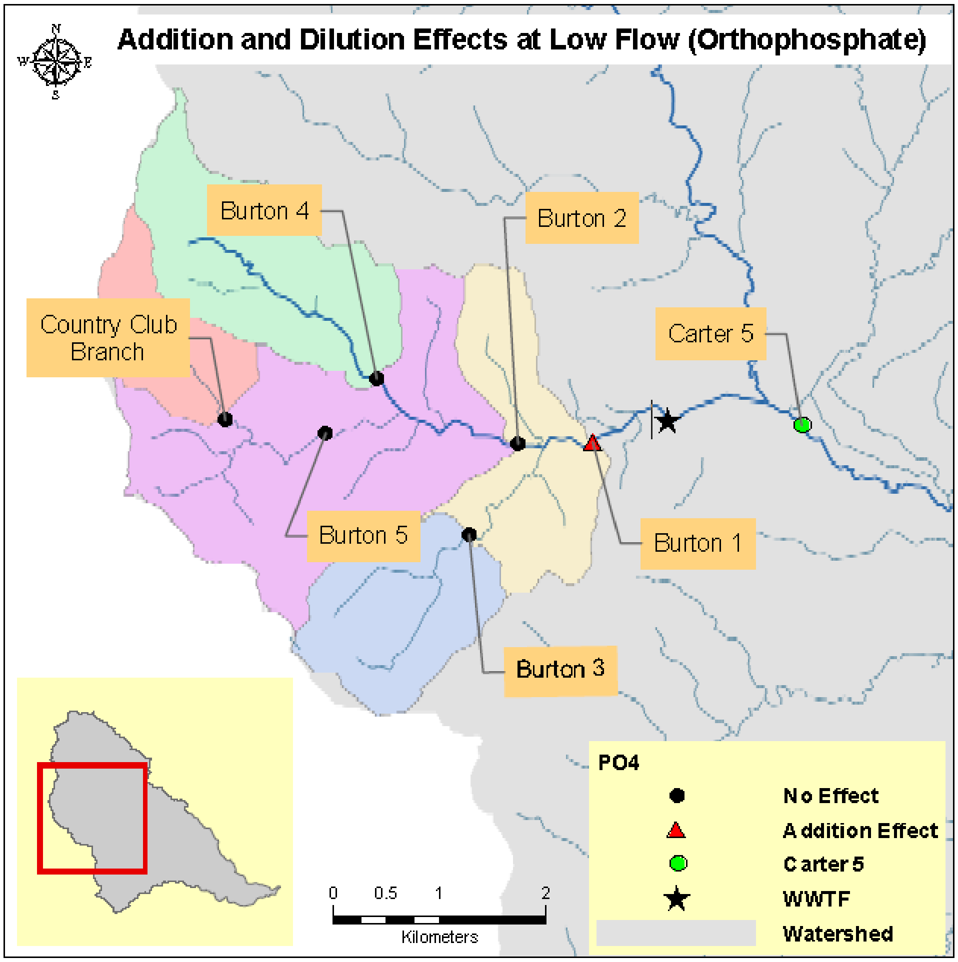


Fig. 2.21 Addition and dilution effects on downstream water quality at low flow (orthophosphate-P)

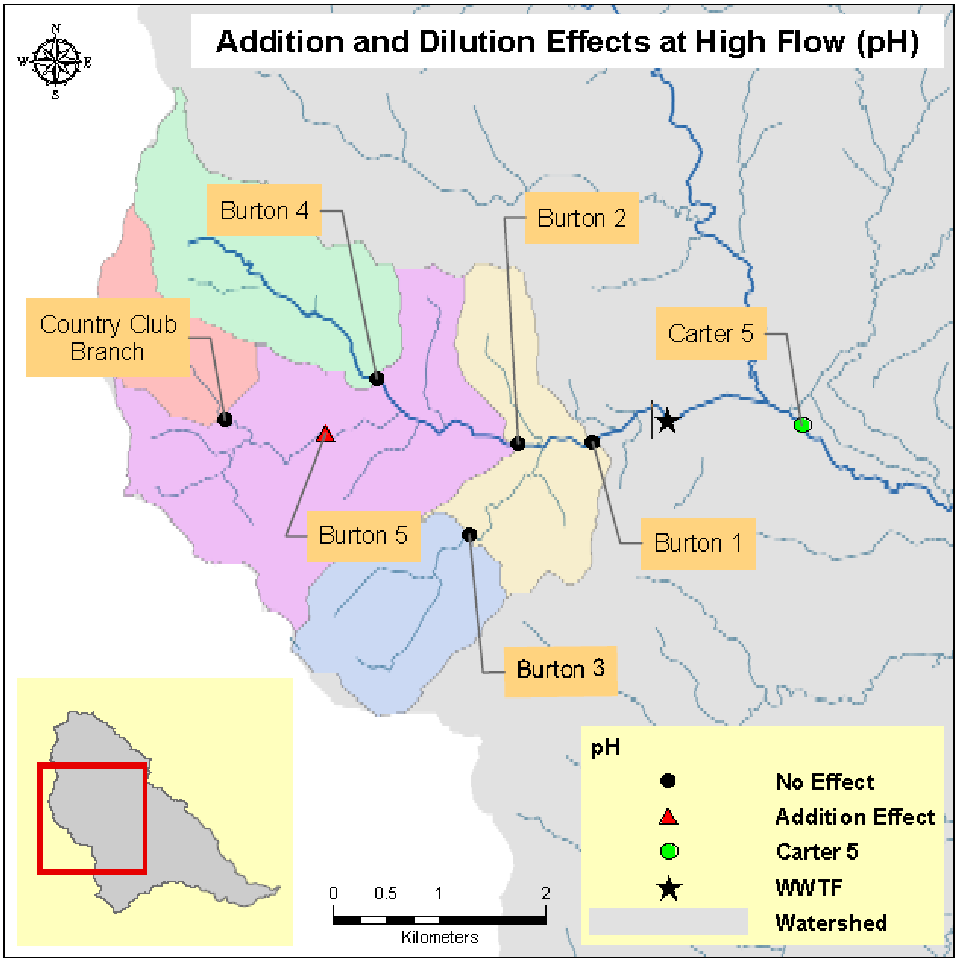


Fig. 2.22 Addition and dilution effects on downstream water quality at high flow (pH)

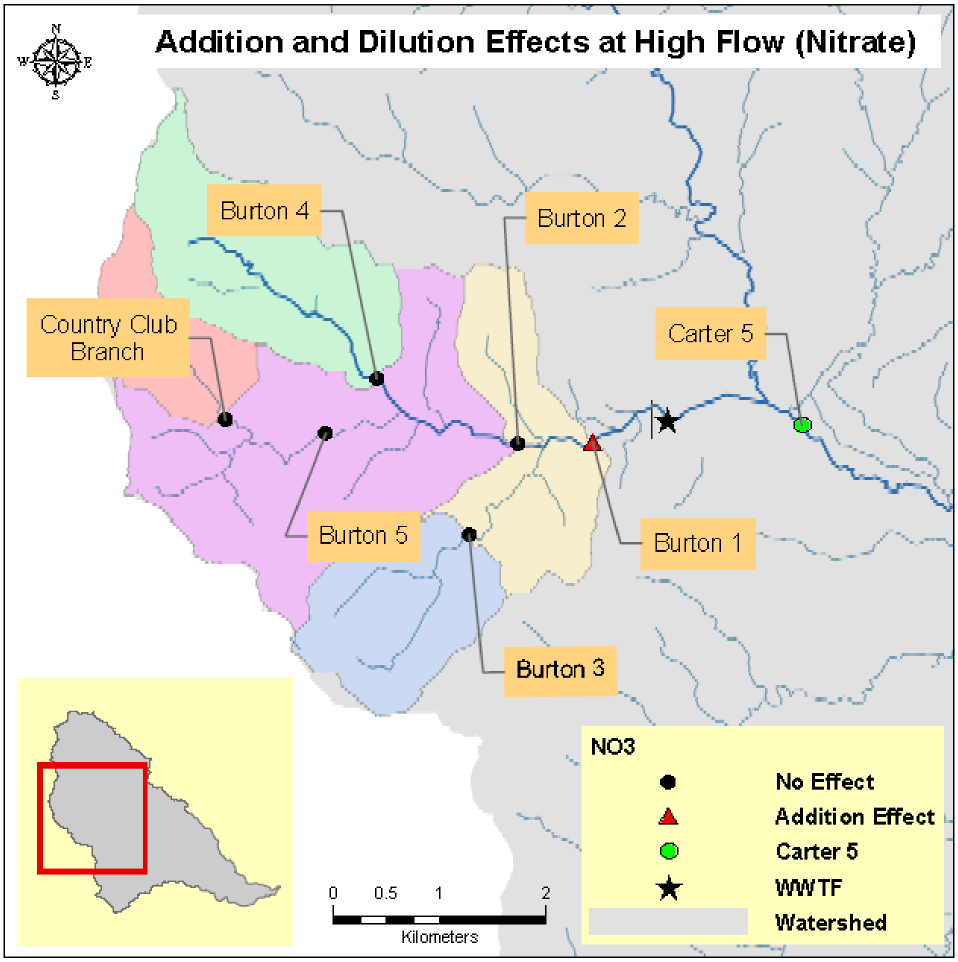


Fig. 2.23 Addition and dilution effects on downstream water quality at high flow (nitrate-N)

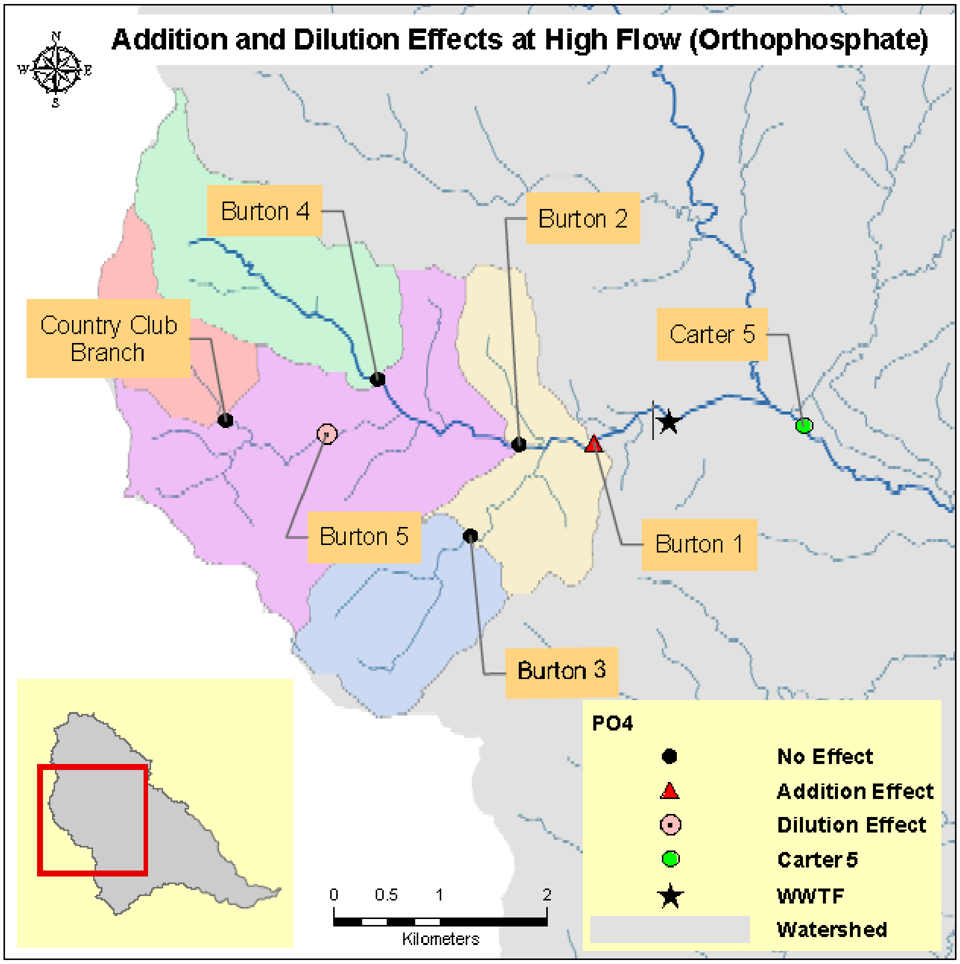


Fig. 2.24 Addition and dilution effects on downstream water quality at high flow (orthophosphate-P)

2.4 DISCUSSION

2.4.1 Effect of High and Low Flow on Carbon, Nitrogen and Phosphorus Concentrations

Stream water is typically derived from baseflow which generally has low nutrient concentrations and storm flow which generally has high nutrient concentrations. Many urban streams are hydrologically disconnected from groundwater and it has been stated that during low flow in urban streams in this region stream water is generally either permitted point source discharge of sewage effluent or irrigation runoff (Aitkenhead-Peterson et al. 2009). Thus, the expectation of lower C, N and P during low flow conditions cannot always be met. One of the major reasons for examining the Carters Creek basin, particularly using this nested design was to examine where hot spots of increased C, N and P might occur. Although no numeric water quality criteria currently exist for N and P, compared to narrative criteria developed for the North Bosque River in central Texas where $P < 0.05$ mg L^{-1} was found necessary for limiting algal growth and maintaining aquatic health (TCEQ 2001), Carters and Burton Creeks have elevated P concentrations. Both Burton and Carters Creek are on the 303d list for impaired waters from excess bacteria surpassing the state water quality standards for primary contact recreation (*E. coli* > 125 cfu). The bacteria, *E. coli* is thought to survive in these urban streams because of the high concentrations of nitrate-N, ammonium-N, orthophosphate-P, DON and DOC that run off the watershed during high flow (McCrary et al. 2013). The results of this study did find some significant differences in these nutrients when comparing high and low flow.

2.4.1.1 pH

Significant differences in pH among some streams when comparing high and low flow were found in this study. Harclerode et al. (2013) noted no significant difference in pH between low and high flow for any stream sampled. In their study during low flow pH ranged from 7.3 to 8.9 and during high flow it ranged from 7.4 to 8.3 compared to 7.7 to 9.4 during low flow and from 7.7 to 9.0 at high flow in this study. It was evident when comparing those streams sampled in 2007/2008 by Harclerode et al. (2013) and the same streams in 2012/2013 that there was an increase in stream water pH five years later. A possible cause for the pH differences is the lower annual rainfall in 2012/2013 compared to 2007/2008. Increased irrigation with high pH sodium bicarbonate municipal tap water is a likely mechanism explaining elevated pH in the watershed streams. Higher annual rainfall in 2007 with low pH contributed to lowered stream pH.

Between 2007 and 2012, the average pH in the streams has increased slightly. The optimum range of desired pH for healthy aquatic systems is 6-9.5 (EPA 2013). Under all flow conditions, this standard was met. If the assumption is made that low flow conditions are dominated by irrigation runoff and not baseflow in these streams then the higher pH in 2012 compared to 2007 makes a lot of sense. If low flow was derived from groundwater, then pH would not be expected to change when comparing the two years. However, if low flow is derived from sodic irrigation runoff during dry summer conditions then it can be expected to show an increase relative natural baseline pH.

Low flow pH in the study streams were similar to those reported for other urban streams such as the Ventura River in California (Klose et al. 2012). Dissimilar results with lower pH (6.6) reported in other studies were attributed to local geologic influences (Clinton and Vose 2005). It is apparent that pH is impacted by multiple factors such as land use, hydrologic connectivity, baseflow chemistry, and watershed geology.

2.4.1.2 Electrical Conductivity

Conductivity is a measure of dissolved ions such as Ca^{2+}, Mg^{2+}, Na^{+}, NO_3^{-} and SO_4^{2-} in stream waters (Steele et al. 2010). Morgan et al. (2007) reported values ranging from 131 to 839 $\mu S\ cm^{-1}$ with increasing watershed urbanization in Maryland. Conductivity in local Texas streams is slightly higher ranging from 292-1198 $\mu S\ cm^{-1}$ at low flow to 218-721 $\mu S\ cm^{-1}$ at high flow (Harclerode et al. 2013). Watershed disturbance gradients are associated with higher specific conductance (Zampella et al. 2007). Consistent with these results, conductivity has been found to correlate strongly with urban impervious cover (Hatt et al. 2004; Morgan et al. 2007). The results of this study support these findings, with higher conductivity measured in the more urbanized Burton Creek watersheds than at the Carter Creek sites.

In this study higher conductivity was observed in all streams under low flow conditions. These differences were prominent during the colder months of the year. Less rainfall leading to lower flow would be expected to concentrate any dissolved ions in stream water, thereby yielding higher conductivity. Typically this would associate with higher N and P also during low flow. However, these elements are derived from surficial watershed sources, therefore higher concentrations would be expected at high flow when these nutrients are flushed from the watershed. Studies have reported irrigation water chemistry may impact nutrient release from urban soils (Aitkenhead-Peterson et al. 2009, 2011). In times of limited rainfall, landscape irrigation is more prominent in arid and sub-tropical regions. This could be another contributing factor to the observed increase in dissolved ions during periods of low flow; particularly if the irrigation water has a high conductivity.

2.4.1.3 Nitrate-N

Nitrate-N concentrations in urban streams tend to be higher than observed in their rural counterparts (Brett et al 2005). Much of this increase is due to point source permitted sewage effluent discharges which are more common in urban and urbanizing watersheds than rural watersheds where there is a tendency toward on-site sewage facilities such as septic tanks. Several studies have reported elevated nitrate-N concentrations downstream of waste water treatment facilities (Aitkenhead-Peterson et al. 2011; Kaushal et al. 2011). This is due to the nature of effluent treatment employed at such facilities. Secondary treatment in wastewater treatment plants reduces the biological oxygen demand of effluent by introducing carbon consuming bacteria in aeration tanks. This process oxidizes nitrogen compounds in the water, producing nitrate-N. Facilities lacking tertiary treatment mechanisms required for eliminating nitrate-N from treated effluent subsequently introduce elevated levels of nitrate-N to receiving waters.

Nitrate-N concentrations in this study were much higher than concentrations reported by Harclerode et al. (2013) in a 2007 study of some of the same streams.

Concentrations of nitrate-N in the Harclerode et al. (2013) ranged from 10.3 mg L^{-1} to 0.048 mg L^{-1} in the upper Carters Creek watershed. Harclerode et al. (2013) reported that their highest concentrations of nitrate-N were downstream of the Burton Creek wastewater treatment plant for all seasons, under all flow conditions. My results demonstrate the same trend in 2012. Concentrations at Carter 5, downstream of the wastewater treatment plant were much higher than in any other creek. Harclerode et al. (2013) also reported higher concentrations of nitrate-N at high flow at Burton 3 and Carter 5 during the winter season.

Increases in nitrogen concentrations in urban streams have also been documented in other studies (Zampella et al. 1994; Wernick et al. 1998). Wernick et al. (1998) documented concentrations ranging from 0.02-7.1 mg L^{-1} in a rural-urban gradient in British Columbia, Canada. In Maryland, concentrations of 0.6 mg L^{-1} to 1.41 mg L^{-1} were reported at urban catchment classifications ranging from 0% to 70% urban (Morgan et al. 2007). The results of this study found much higher concentrations of nitrate-N ranging from 0.02 mg L^{-1} to 22.8 mg L^{-1}. These results however are skewed by the presence of the wastewater treatment plant. Excluding measurements downstream of the facility, nitrate-N concentrations in this study ranged from 0.02 mg L^{-1} to 0.72 mg L^{-1}. These results are similar to the other published studies.

Shifting urban landscapes alter hot spots for nutrient cycling (Grimm et al. 2009). Locations which gather and retain flowing water for periods of time such as stormwater detention basins and grassy swales were suggested to be new areas for denitrification of nitrate-N in urban landscapes (Groffman et al. 2003) replacing traditional riparian function. The location of such areas will certainly shift nutrient loadings within subwatersheds.

2.4.1.4 Ammonium-N

Observations of ammonium-N in surface waters are quite rare unless the stream or river is receiving untreated sewage such as the Bagmati River in Nepal (Bhatt and McDowell 2007). Typically stream water concentrations of ammonium-N are quite low. Triska et al. (1994) reported concentrations < 0.01 mg L^{-1} in the New Jersey Pinelands and Aumen et al. (1986) found <0.005 mg L^{-1} ammonium-N concentrations in temperate ecosystems of the Pacific northwest. Higher ammonium-N concentrations (0.02-0.04 mg L^{-1}) were documented along a rural-urban gradient by Brett et al. (2005). This may be indicative that disturbances to typical watershed mechanisms are introducing ammonium-N to surface waters in urban areas.

Three streams in this study (Burton 5, Carter 1, and Carter 2) had significant differences between high and low flow ammonium-N concentrations with higher concentration at high flow. Average concentrations (0.19-1.71 mg L^{-1}) more closely matched those reported by Brett et al. (2005) than those in rural studies (Triska et el. 1994; Aumen et al. 1986). Re-suspension of sediments with adsorped ammonium-N in urban streams may explain why slightly higher concentrations were observed at high flow. Channelized streams such as Burton Creek gather allochthonous sediments which are then deposited in the channel when flow is slow. Visual assessment of streams in the study during fieldwork confirmed sediment accumulation along channelized stream banks (Fig 2.25). Sediment re-suspension during storm events therefore may have caused higher ammonium-N concentrations in my study as compared to other studies (Triska et al. 1994).

In 2007, Harclerode et al. (2013) found no significant differences in ammonium-N among any of the streams they studied. This finding supports the theory that surface water chemistry is changing in these streams over time and with increasing urbanization. One reason for this may be the particularly dry summer in 2012 compared to 2007 when more irrigation was used. Irrigation with water high in sodium ions may displace ammonium-N from soil exchange sites. Alternatively, ammonium may be displaced from the watershed attached to soil particles through erosion of watershed soils. A study in Humbolt County, California identified transient adsorption to sediments as an important storage pool for ammonium. Ammonium-N concentrations were higher during high flow conditions compared to low flow conditions which may have been due to disturbance of sediment in the channel releasing ammonium-N sorbed to sediments to the water column.

Concentrations of ammonium-N in this study were higher than Harclerode et al. (2013) both at low and high flow. The authors documented that ammonium-N ranged from 0.03 to 0.17 mg L^{-1} during low flow and from 0.05 to 0.15 mg L^{-1} during high flow compared to the annual range of 0.19-1.71 mg L^{-1} in my study.

Fig. 2.25 Deposition of allochthonous sediments in channelized creek (Burton 4, November 25th 2012)

Ammonium-N in stream sediments typically results from bacterial decomposition of autochthonous organic matter inputs into streams (Harmon et al. 1986). A lack of oxygen in typically anaerobic stream sediments prevents nitrification of mineralized organic matter from occurring. Nitrogen species in anaerobic sediments are therefore higher in concentration in the form of ammonium-N than as nitrate-N or nitrite-N (Triska et al. 1994). Field observations indicated at minimum two riparian clear-cutting events (Fig 2.26) in the one year sampling period at Country Club Branch (CCB). Also, slow moving water was routinely observed at this particular site. Regular riparian de-vegetation introduces a lot of organic matter to the creek and possibly explains why highest ammonium-N concentrations were found here. Slower stream flow due to this obstruction further limits aeration of creek sediments, thereby resulting in high ammonium-N concentrations. This recruitment of coarse woody debris (CWD) into the stream will have an effect on nitrogen speciation both in the sediments and in stream water (Aumen et al. 1985; Harmon et al. 1986). The decomposition rate of ^{14}C-lignocellulose was found to be affected by ambient nitrate-N and ammonium-N concentrations in a study by Aumen et al. (1985). An accumulation of organic N in wood samples was observed coupled with enrichment of ammonium-N in solution in the presence of supplemental nitrate-N. It is therefore evident that the introduction of coarse woody debris into streams can result in elevated ammonium-N and lowered nitrate-N in-stream concentrations.

Fig. 2.26 Organic matter inputs into creek as result of riparian clear-cutting (Country Club Branch, November 25th, 2012)

2.4.1.5 Orthophosphate-P

Orthophosphate-P is a key nutrient for aquatic health and has been identified as the most limiting nutrient in freshwater systems (Paul and Meyer 2001). Urban streams experience unique landscape inputs of orthophosphate-P which differ from rural sources (Steele et al. 2010). Contributions from asphalt parking lots (Hope et al. 2004), urban land use (Brett et al. 2005), and waste water treatment plants (Aitkenhead-Peterson et al. 2011; Carey et al. 2009) have been cited as distinctly urban sources of orthophosphate-P.

Clinton and Vose (2006) found orthophosphate-P concentrations ranging from 0-1.39 mg L^{-1} in urban streams. A similar range of concentrations (0.07-1.02 mg L^{-1}) was reported in simulated storm runoff from asphalt parking lot surfaces (Hope et al. 2004). Comparisons with less disturbed forest streams have shown urban counterparts to have as much as 122% higher orthophosphate-P concentrations (Brett et al. 2005). Studies in urban watersheds with (Ekka et al. 2006) and without waste water treatment plants (Bhatt and McDowell 2007) have reported even higher concentrations of 2.1 and 3.0 mg L^{-1}, respectively. These findings suggest that urbanization alters typical nutrient cycling mechanisms due to which greater orthophosphate-P transport occurs in urban watersheds.

In this study orthophosphate-P concentrations were higher during high flow than at low flow at most streams. This could be attributed to elevated erosion from the landscape and sedimentation in stream water following rain events. Since orthophosphate-P is mostly transported adsorped to sediments (Paul and Meyer 2001; Steele et al. 2010), elevated flow likely re-suspended sediments settled on creek beds.

Alternatively, orthophosphate-P removed from the watershed either by soil erosion or removal of dusts from impervious surface areas would also account for higher concentrations of orthophosphate-P in urban streams. Landscape disturbance has previously been found to elevate orthophosphate-P concentrations in urban streams (Clinton and Vose 2006).

Burton 2 and Carter 5 had much higher orthophosphate-P concentrations than the other streams at low flow. This could be attributed to a large urban commercial strip with extensive parking lots in the watershed. Hope et al. (2004) reported elevated orthophosphate-P concentrations from asphalt in a commercial setting (0.30 mg L^{-1}) relative to asphalt in residential and light industrial settings (0.13-0.18 mg L^{-1}). Harclerode et al. (2013) found a similar pattern with positive orthophosphate-P correlations with commercial land use (low flow R=0.23, high flow R=0.39). Increased runoff from such impervious surfaces in commercial areas carrying orthophosphate-P sorbed sediments is therefore a possible mechanism for elevated orthophosphate-P at Burton 2 at low flow. This pattern however was not observed during high flow, which is possibly a result of dilution.

Highest orthophosphate-P concentrations were measured downstream of the wastewater treatment plan at Carter 5 (1.8-3.6 mg L^{-1}). These results support the findings of Harclerode et al. (2013), who also reported highest orthophosphate-P concentrations in the watershed (1.7-2.7 mg L^{-1}) downstream of the wastewater treatment plant. Concentrations found in this study were similar, but slightly higher than those reported in other urban streams. Ekka et al. (2006) found higher orthophosphate-P concentrations downstream of WWTP effluent discharges (0.08-2.10 mg L^{-1}) compared to upstream (0.02-0.12 mg L^{-1}). These results make sense since waste water treatment plants are categorized as point sources of phosphorus (Carey et al. 2009).

Interestingly my results are quite similar to Bhatt and McDowell (2007) who reported mean concentrations of 3 mg L^{-1} in stream water receiving untreated domestic sewage as well as industrial and agricultural effluent inputs in the Bagmati River in Nepal. This indicates that the Burton Creek watershed supplies high orthophosphate-P to Carters Creek despite the presence of a WWTP. Without an appropriate regulatory environmental standard for orthophosphate-P (TCEQ 2012), high concentrations will continue to be routinely discharged into Carters Creek.

2.4.1.6 Dissolved Organic Carbon

DOC concentrations typically increase in streams during high flow as a response to the interaction of precipitation with watershed vegetation and soils (Aitkenhead-Peterson et al. 2003). Supporting results found in urban streams in Phoenix, AZ where DOC concentrations increased in response to runoff events (Westerhoff and Anning 2000). Hope et al. (2004) reported mean concentrations of 47.6, 81.2, and 59.1 mg L^{-1} in high flow runoff from light industrial, commercial and residential parking lots. DOC concentrations in this study however were higher at low flow than at high flow, which does not support this general consensus. Harclerode et al. (2013) also reported higher DOC concentrations at low flow relative to high flow and for the most part displaying no significant difference in DOC concentrations between high and low flows. Dilution of

DOC concentrations during a wet 2007 may be the reason for Harclerode et al. (2013) results of similar DOC concentrations during high and low flow.

Typical response to flow conditions generating higher DOC concentrations at high flow is governed by the assumption of regular hydrologic flow paths. Groundwater sources are typically lower in DOC whereas DOC emanating from upper soil horizons during storm flow is higher in concentration (Hook and Yeakley 2005; Sickman et al. 2007). Disconnected hydrologic flowpaths in urban areas (Grimm et al. 2009) may negate the influence of baseflow on water chemistry. Flow in Carters Creek is dominated by effluent discharge and irrigation runoff during warm months. As such, low flow conditions are influenced strongly by irrigation water chemistry and effluent composition (Aitkenhead-Peterson et al. 2009). Studies have shown irrigation of open urban areas with high sodium water to result in increased DOC loss from soils (Aitkenhead-Peterson et al. 2009; Cioce and Aitkenhead-Peterson 2013). Irrigation with municipal tap water high in sodium is believed to induce sodic soil conditions resulting in elevated DOC (Pannkuk et al. 2011). Leaching of DOC from soils is impacted by irrigation water quality (Steele and Aitkenhead-Peterson 2012) which is a possible explanation why higher DOC concentrations were found at low flow when stream flow is mostly because of irrigation. In addition, DOC concentrations may be lower during high flow as a result of dilution.

Relative to other urban streams, the results of this study indicate higher mean DOC concentrations. Concentrations similar to those in forested watersheds (1.8-3.1 mg L^{-1}) by McDowell and Likens (1988) were found (2.0-4.1 mg L^{-1}) by Hook and Yeakley

(2005) in a small urban stream in Oregon. A larger range (0-13 mg L^{-1}) was reported by Westerhoff and Anning (2000) for streams in Arizona. My results were much higher than these findings, with concentrations of 37.4 to 54.0 mg L^{-1}at high flow and 23.0 to 68.0 mg L^{-1} at low flow. The differences between these findings suggest a mechanism at play in the Carters Creek watershed which is resulting in elevated DOC in runoff. This is likely due to leaching of DOC from urban soils due to continued irrigation with high sodium water. Road splash from deicing salts (NaCl) in Great Britain resulted in total loss of soil carbon over time (Green et al. 2008) and there is a potential for this to happen in Carters Creek basin soils with continued sodic irrigation.

2.4.1.7 Dissolved Organic Nitrogen

DON is a byproduct of living organisms. An increase in bioavailable DON in human-dominated surface waters has resulted in increased interest in study of DON dynamics (Pellerin et al. 2006). Typical urban stream water DON concentrations are quite low although concentrations as high as 6.13 mg L^{-1} have been found in streams receiving raw effluent (Bhatt and McDowell 2007). Pellerin et al. (2006) reported mean concentrations varying from 0.02 to 3.20 mg L^{-1} across a rural-urban gradient in north-eastern USA with higher concentrations in urban streams. Urban watershed streams therefore experience higher DON concentrations than rural forested watershed streams. Pellerin et al. (2006) documented urbanization as a cause of elevated DON in urban streams. This is because of both point source pollution such as WWTPs and non-point source losses from soils. Significantly higher losses of DON were observed from urban park soils relative to remnant native soils were found in south-central Texas (Aitkenhead-Peterson and Cioce

2013). WWTPs are also regularly cited as sources of DON to urban waters (Lewis et al. 2007; Carey et al. 2009). Lewis et al. (2007) found higher DON concentrations downstream of a WWTP (0.89 mg L^{-1}) than in upstream urban streams (0.10 mg L^{-1}) in the Big Brushy Creek watershed in South Carolina.

DON concentrations in my study were higher than those found in other urban streams. Concentrations ranged from 0.47-2.88 mg L^{-1} at low flow to 0.94-1.99 mg L^{-1}at high flow. A similar range of DON concentrations were reported by Harclerode et al. (2013), 0.58-3.29 mg L^{-1} at low flow and from 0.76-1.17 mg L^{-1} during high flow. Lower concentrations at high flow were likely due to DON flushing from soils during rain events and dilution. It has been suggested in the literature that DON dynamics are not regulated by traditional biotic mechanisms, but rather by a complex set of factors which may be sensitive to availability of inorganic-N (Pellerin et al. 2006). Higher watershed N concentrations were positively correlated to higher DON concentrations in the Pellerin et al. (2006) study. In this study higher ammonium-N concentrations were found at high flow. DON concentrations however were higher during low flow conditions.

Point source discharges from WWTP in urbanizing catchments contribute DON to receiving waters (Pellerin et al. 2006; Carey et al. 2009). In this study, highest DON concentrations were found downstream of the WWTP. Similar results were found by Harclerode et al. (2013) and Lewis et al. (2007). These findings support the argument that WWTP discharge is a significant point-source contributor of DON to urban surface waters.

2.4.2 Effect of Climate on Stream Nutrient Concentrations

Climate is known to impact nutrient cycling both directly through higher water temperatures and indirectly with greater presence of aquatic plants and animals (Steele et al. 2010). A review by Pickett et al. (2001) determined that removal of riparian vegetation, decreased groundwater recharge, and the "urban heat island" effect associated with urbanization resulted in altered heat budgets. Warmer temperatures are known to increase algal growth (Anderson et al. 2003) thereby increasing nutrient uptake from surface waters. It was expected that stream N and P would therefore be lower in the warmer months as opposed to colder months. Significant differences in water quality however were only found for ammonium-N at Carter 5 and for DON at Briar 2. Seasonal trends in water quality were difficult to disaggregate into four seasons as done in Harclerode et al. (2013) due to lack of samples. Because of no flow in some of the streams during the summer months, stagnant water samples taken were removed from analysis which limited the number of samples remaining.

Although few significant differences were found in seasonal analysis, some patterns were observed. Lower nitrate-N and orthophosphate-P concentrations were found during the hot season than during the cold season. This result supported my hypothesis which stated that uptake of nutrients by aquatic biomass is a possible mechanism reducing hot season N and P concentrations. The lack of strong seasonal patterns in my data indicated that seasonality is not as strong a driving force affecting urban aquatic chemistry as flow conditions or land use.

2.4.3 Effect of Land Use on Stream C, N and P Concentrations

Land use and land cover (LULC) change has significant direct and indirect effects on watershed biogeochemistry. Landscape metrics are therefore commonly used to spatially evaluate nutrient loadings and watershed health (Hope et al. 1994; Wernick et al. 1998; Brett et al. 2005; Aitkenhead-Peterson et al. 2007; Morgan et al. 2007; Aitkenhead-Peterson et al. 2009; Kaushal et al. 2011). Percent land use is the most frequently used landscape metric correlated with stream chemistry. In particular, percent urban land use is the focus of many studies for evaluating various nutrients such as nitrate-N (Morgan et al. 2007; Zampella et al. 2007; Kaushal et al. 2011), orthophosphate-P (Brett et al. 2005), DOC (Aitkenhead-Peterson et al. 2009), and DON (Pellerin et al. 2006). Spatial patterns such as the land use closest to a monitoring site, rather than aggregate land cover in the watershed have been implied to most strongly impact water quality degradation on a local scale (Zampella et al. 2007). This is the reason a nested approach was utilized in this study to determine the impacts of different land uses on stream water chemistry.

For the purpose of this study, land use meant the category best defining an area's particular ecology. For example, urban land use includes all watershed areas association with human-dominated uses such as open urban spaces, commercial, residential, and industrial land uses. I used widely accepted LULC classifications from the National Land Cover Database, 2006.

Urban streams typically have higher concentrations of most nutrients relative to rural streams (Morgan et al. 2007). Interruption of hydrologic connectivity and traditional flow paths disturbs nutrient cycling, particularly N (Grimm et al. 2004). Decreased channel complexity was found to increase aquatic primary productivity and subsequent N concentrations (Grimm et al. 2005). The amount of impervious surface and drainage networks within urban watersheds are then quite an important variable effecting urban hydrology and stream chemistry. Disturbance of riparian functioning also strongly effects nutrient retention, transformation, and release (Harmon et al. 1986). This leads to a shift in wildlife behavior such as fecal deposition from avian sources which add to nutrient loads in urban areas (Fujita and Koike 2009).

Comparisons of stream chemistry along rural-urban gradients have found higher nitrate-N concentrations in urbanizing watersheds than in forested watersheds (Brett et al. 2005; Kaushal et al. 2011). Possible sources suggested for this correlation were wastewater from septic systems and lawn fertilizer (Kaushal et al. 2011). On the other hand, denitrification in urban storm drain networks in the presence of labile organic carbon, decreased light in subsurface concrete-lined drains, wet conditions and sufficient water residence time between storms was also suggested to reduce baseflow nitrate-N (Kaushal et al. 2011). Brett et al. (2005) reported no significant correlation between % urban land cover and nitrate-N and ammonium-N concentrations (R^2=0.16, R^2=0.21). In this study no significant correlations were found with nitrate-N, or DON to any watershed land use. Likely the lack of septic systems in the watersheds sampled and influence of healthy riparian zones of the Carter sites led to this result.

Orthophosphate-P adsorbs strongly to soil particles. With increased turbidity in urban areas (Brett et al. 2005), it makes sense that increased erosion and soil disturbance may result in elevated urban orthophosphate-P concentrations. In this study orthophosphate-P showed negative correlations with range, barren, and wetland land uses during high flow and positive correlations with range and barren during low flow. These results differ from Harclerode et al. (2013), who found no significant correlations of P with any land uses in the Carters Creek watershed in 2007. This difference is most likely due to increased urban growth in the watershed since 2007. Areas previously designated as range and barren have been since developed in the headwater areas of Carters Creek. The lack of up to date land use and land cover (LULC) maps however make this theory difficult to test. LULC data used in the analysis is outdated (2006), which probably affected my results. Orthophosphate-P was one of two nutrients in the study which showed significant correlations to land use in the headwaters of Carters Creek basin where it was observed that high sediment loads were present in the water column during high flow. Other authors have also found that orthophosphate-P correlated positively ($r = 0.56$) with % urban land cover (Brett et al. 2005). As the results of many studies show, urbanization directly leads to elevated orthophosphate-P concentrations. In this study, this is due to increased construction and poor management practices such as dysfunctional silt fences preventing sediment loading to Carters Creek to cope with the rapid urban growth in the basin.

Recent studies have shown significant positive correlations between DOC concentrations and proportion of high density, open area land use (Aitkenhead-Peterson et al. 2009; Steele et al. 2012). In this study, DOC correlated significantly ($R= 0.71$, $p<0.05$) with urban land use. This is indicative that mechanisms resulting in elevated

DOC loss from urban areas exist. This theory is supported by Kaushal et al. (2011) who found that elevated DOC concentrations from storm drains had a watershed origin. Harclerode et al.2013 also reported a relatively high, but insignificant correlation of DOC with commercial land use both during low and high flows (low flow R=0.59, p=0.09 and high flow R=0.60, p=0.09). It is interesting to note that DOC did not significantly correlate with urban land use in 2007, but did in 2012. It indicates an increase in DOC concentrations and urban land use in the watershed over time. Some studies have claimed losses from soil contribute strongly to elevated DOC concentrations (Aitkenhead-Peterson and Cioce 2013; Cioce and Aitkenhead-Peterson in review). Local irrigation of urban open areas such as golf courses, athletic fields and parks with water high in sodium is thought to cause result in sodic soils. Increasing sodicity leads to the dispersal of soil aggregates, clays and organic matter and introduce pathways for DOC mobilization from soil sites. Reactive soil pools and losses are higher in urban relative to remnant soils (Aitkenhead and Cioce 2013) and competition on anion exchange sites from bicarbonate is not yet proven. Sodic irrigation also affects soil microbial community composition (Holgate et al. 2011) which in turn may reduce the microbial mineralization of DOC which has been observed in urban relative to remnant soils (Cioce and Aitkenhead-Peterson in review).

Overall, land use is a broad category with which to correlate nutrient loads. Urban landscapes contribute higher nutrient concentrations than undisturbed ones, but the mechanisms controlling biotic and abiotic processes within land uses are highly complex and variable, especially for coupled elemental cycles. Finer scale analysis is required to truly disaggregate the influence of land use on nutrient concentrations.

2.4.4 Identifying Hot-Spots in a Nested Study

Nested watershed approaches have recently emerged as a powerful technique for addressing environmental concerns such as non-point source pollution (Harclerode et al. 2013). GIS based tools enable greater visualization and analytical capacity for spatial identification of problem areas. In this study, a nested design was used to enable identification of key areas of C, N or P loading in the Burton Creek watershed. Statistical analysis of water quality of downstream sites with those directly upstream was conducted for in-depth examination of C, N and P variation at localized scales.

As described earlier, landscape metrics are important for identifying key locations for nutrient loadings in watersheds. For example, Fujita and Koike (2009) identified higher avian nutrient loadings to fragmented urban forests than to forested watersheds. This suggests the location of certain land uses and their continuity, a landscape metric, can affect nutrient loadings to them. The relationship between subwatersheds and localized land use was tested in this study. It was assumed that higher concentrations at upstream sampling locations than sites just downstream of them were a result of dilutions and the opposite, an effect of addition of nutrient loads. Some studies have attempted to create predictive nutrient loading models using landscape metrics as model parameters (Jones et al. 2001; Brett et al. 2005). The format of such studies is somewhat different than mine because they use regression analysis with metrics to identify the most useful metrics explaining water quality. Although a useful approach for describing key mechanisms influencing nutrient exports, it lacks the ability to pinpoint problem areas spatially.

In my results, more significant differences in water chemistry between streams were found at low flow than high flow. Prominent variation was between pH, EC, nitrate-N and orthophosphate-P. Since higher concentrations for these parameters were found during low flow, it is likely that greater variability caused the differences found. All significant differences for all parameters except EC at Burton 3 relative to Burton 1 were due to addition effects at low flow, regardless of their location in the Burton creek watershed. This indicated that at low flow, nutrients progressively accumulated from headwaters to downstream locations in the watershed.

Country Club Branch (CCB) relative to Burton 5 had significant lower pH and EC at low flow. A large municipal golf course located between the two sites could possibly explain this. Soils regularly irrigated with high sodium water leach cations such as K^+, Na^+, Ca^{2+} and Mg^{2+} which are displaced from soil binding sites during cation exchange. An increase in alkalinity would increase pH as well as dissolved anions in stream water to maintain electroneutrality resulting in increased conductivity. At low flow, irrigation is typically the primary source of overland flow to urban streams (Aitkenhead-Peterson et al. 2009).

Differences between Burton 1 and 2, and Burton1 and 3 helped identify watershed loading of nitrate-N during low flow. Both Burton 2 and 3 are upstream of Burton 1, however only Burton 1 had lower nitrate-N concentrations relative to Burton

3. Therefore, the Burton 3 watershed can be identified as a source of impairment causing elevated pH, EC, and nitrate-N at Burton 1 during low flow. Contributions from Burton 2 and upstream watersheds are hence insignificant. The reason for higher nitrate-N at Burton 3 may be due to increased fecal pollution from pets and wildlife. A study of avian fecal contributions in Japan identified birds as active vectors of nutrient transport to fragmented urban forests (Fujita and Koike 2009). The Burton 3 watershed has greater fragmented urban forest cover than in the other sub-watershed. Also, many urban parks and trails for recreation in the sub-watershed are frequented by pet owners. Input of nutrients from fecal matter is a possible mechanism for elevated nutrient loads observed.

The most interesting pair in the study was Burton 1 and Carter 5 which have a waste water treatment plant (WWTP) outfall between them. Carter 5 had significantly higher values (α=0.01) for pH, EC, nitrate-N and orthophosphate-P at low flow. At high flow the differences were also highly significant (α= 0.01), but only for nitrate-N and orthophosphate-P. These two parameters were also noted in Harclerode et al. (2013) to be elevated downstream of Burton 1. It is important to note that the relationship between water chemistry and additive influences from the WWTP between the two locations remained unchanged from 2007 to 2012. This suggests a consistent input of N and P in this area of the watershed is present. Harclerode et al. (2013) attributed elevated N and P concentration to the WWTP between the sampling locations. The City of Bryan WWTP provides only primary and secondary treatment to effluent before releasing it into Burton Creek (TCEQ 2009). Given the lack of tertiary treatment in the Burton creek WWTP to remove nitrate-N and orthophosphate-P, it is not a surprise that these nutrients are consistently higher downstream of the WWTP than ambient creek concentrations. Furthermore, the plant does not have effluent concentration limitations or monitoring requirements for either nitrate-N or orthophosphate-P (TCEQ 2009). The results of this study support the findings of Harclerode et al. (2013) and indicate a need for greater monitoring of point sources in the Carters Creek watershed.

The nested design used in this study allowed for spatial disaggregation of N and P sources in an urban basin. Combined with local watershed knowledge, this can aid in identification of loading 'hot spots'. Furthermore, this technique can pinpoint problem areas where greater monitoring and management efforts can be applied in the future to identify exact sources and focus mitigation efforts. This design would benefit from flow data for the streams that were sampled so that nutrient loads could be calculated. Nutrient loadings are more informative indicators of addition and dilution effects than concentrations alone.

2.4.5 Limitations to Study and Recommendations for Future Work

Due to only sampling these streams once each month, the study was limited in the number of samples to examine seasonal high and low flow nutrients. Furthermore, some of the headwater streams which were accessible due to new development tended to be dry for several months of the year or, the water was stagnant and not flowing so that a sample could not be used in analysis. Future work should adopt a bi-weekly sampling procedure to enable greater seasonal analysis and to provide a larger sample size for better statistical power.

Outdated land use data from 2006 was used in this study due to the lack of more recent data which is due to be published in December 2013. Many new developments have been constructed in the watershed, particularly in the headwaters of Carters Creek since 2006. This limitation is likely to have affected the result of land use correlation with water quality. Publication of this study should use NLCD 2012 data when it is released. Analysis with local zoning datasets rather than NLCD was not opted for in this study, however local zoning datasets could better help ascertain land uses contributing diffuse nutrients to the streams.

A lack of knowledge about septic system location and status was a significant limitation to this study. Leaky septic systems are reported in the literature to be a major source of nutrients to surface waters (Paul and Meyer 2001). The areas which were sampled were predominantly urban therefore it was assumed septic system influences would be negligible. However, older parts of the city may still have on-site sewage facilities (OSSFs) installed contributing to non-point source nutrient pollution. Identifying the location and status of these OSSFs would certainly enhance conclusions drawn from monitored water quality.

2.5 CONCLUSIONS

Identifying sources of diffuse pollution in urban watersheds is a challenging task. Urban systems are unique in their characteristics and nutrient cycling mechanisms. Source pathways for retention, transport, and conversion are complicated by a variety of physical, chemical, and biological drivers. Impact of human activity on landscape features is visible through the results of this study. Higher nitrate-N, orthophosphate-P, and DOC concentrations were found across the watershed than in 2007. Increased erosion due to construction and soil disturbance by dispersive sodium characteristics (Steele and Aitkenhead-Peterson 2012) are apparent in DOC, DON, ammonium-N and orthophosphate-P concentrations. Land management practices therefore clearly affect surface water quality. Other factors such as land use and flow conditions were also found in this study to impact C, N and P concentrations. Especially noteworthy is the distinct impact of point-source pollution (WWTP) on nitrate-N and orthophosphate-P concentrations. Seasonality had minimal impact on C, N and P concentrations.

Maintaining good surface water quality is important for human and aquatic health. Interactions between land management practices, nutrients, and microbial re-growth have been shown in this study to influence nutrient concentrations in surface waters. The combined influence of these variables on water quality must be assessed in greater detail to identify sources and critical loading areas across the watershed. With detailed spatial knowledge of problem areas, appropriate management efforts can be implemented.

CHAPTER III

SOURCE TRACKING DOC IN STREAMS USING DIFFUSE NEAR-INFRARED SPECTROSCOPY

3.1 INTRODUCTION

Carbon dynamics are understood to have significant importance at global (Schlesinger and Melack 1981; Aitkenhead and McDowell 2000) as well as local (Aitkenhead-Peterson et al. 2007) scales. Carbon is an important source of energy for microbes (Anderson et al. 2002; McDowell et al.2006; McCrary et al. 2013). As such, it is essential for the health of both terrestrial and aquatic ecosystems. Its presence in excess however can pose a threat both to aquatic (Paul and Meyer 2001) and human health (Chu et al. 2002). The majority of studies investigating carbon on a watershed scale have been conducted in relatively undisturbed forested landscapes in temperate regions (Kalbitz et al. 2000 review). Few studies have looked at human impacts on watershed scale aquatic carbon dynamics (Westerhoff and Anning 2000; Hook and Yeakley 2005; Sickman et al. 2007; Aitkenhead-Peterson et al. 2009; Petrone 2010) illustrating a dearth of knowledge in this field.

Urbanization has been found to significantly alter typical loadings of nutrients, metals, pesticides, and other contaminants to streams (Hope et al. 2004; Steele et al. 2010). A greater concentration of impervious surfaces and heightened soil disturbance and compaction increase surface runoff and alter hydrological flowpaths (Paul and Meyer 2001). Aitkenhead-Peterson et al. (2009) reported that land management practices may influence carbon retention in soils. The authors suggested irrigation water chemistry contributed to DOC loss from urban soils in open area such as athletic fields, golf courses, and parks. Further investigation into this theory found that reactive soil pools of DOC were significantly higher in urban relative to rural or remnant soils which would potentially increase DOC loading to surface waters (Aitkenhead-Peterson and Cioce 2013). The DOC in urban soils is also more refractory and less likely to be utilized by the soil microbial community than DOC in rural and remnant soils (Cioce and Aitkenhead-Peterson in review) which will also contribute to higher DOC loading to surface waters.

Identification of pollutant loads to impaired waters is a key element of federally mandated watershed management (EPA 2013). Estimating this loading in watersheds supports future management planning and targeting of restoration activities by watershed planners. Source tracking methods to date have focused on disaggregating hydrologic sources of water using a variety of techniques such as end-member mixing analysis (Christopherson and Hooper 1992), fluorescence (McKnight et al. 2001), neural networks (Clair and Ehrman 1998; Aitkenhead et al. 2007), isotope analysis (Peterson and Howarth 1987; Cioce et al. in review), and gel filtration (Bishop et al. 2004). Some of these methods related carbon concentrations in source waters such as groundwater, the riparian zone, and deep ground water (Christopherson and Hooper 1992) to stream chemistry via proxy measurements. Other studies distinguished between carbon originating from microbial metabolites or that from vegetation (McKnight et al, 2001; Bishop et al. 2004; Peterson and Howarth 1987) and others utilized soil forming factors to estimate DOC exports from watersheds in Scotland (Aitkenhead et al. 2007). Although providing useful insight into possible watershed components contributing carbon to surface waters, all of these methods fall short in specific watershed source identification. The most common method of illustrating sources of DOC to surface waters so far has been simple linear regression analysis with soil type or characteristics or land use (e.g. Aitkenhead et al. 1999; Aitkenhead-Peterson et al. 2007). However, while this method can illustrate that as a certain soil type or characteristic or land use increases in a watershed so will DOC exports, it falls short when trying to identify sources of DOC in urban and mixed land use watersheds.

Near-Infrared spectroscopy has only recently emerged as a possible mechanism for watershed scale carbon determination in mixed land use watersheds (Aitkenhead-Peterson et al. in review). A recent study showed that surface water DOC concentrations can be predicted using an evaporation technique followed by analysis using diffuse reflectance near infrared spectroscopy (Aitkenhead-Peterson et al. in review). Using a full cross validation after partial least square regression analysis, the measured and predicted DOC concentrations were strongly and significantly related ($R^2 = 0.98$ $p < 0.0001$). A further test, to identify specific functional groups important in predicting DOC concentrations using backward multiple regression analysis resulted in an R^2 of 0.998 ($p < 0.001$) with 52 individual wavelengths identified as important predictors of DOC. Finally, the 16-stream validation set (not used in the calibration model) utilized in the study also showed a strong relationship between measured and predicted DOC concentrations ($R^2 = 0.98$; $p < 0.0001$) for DOC concentrations ranging from 8.03 to

52.16 mg L^{-1}. For my research, I wanted to take this methodology a step further by using the spectral signatures obtained from extracted watershed components such as turfgrass, forest leaf litter, soil, runoff, and fecal matter to compare against spectral signatures of stream water chemistry as an aid to determining specific sources of DOC from watersheds.

3.2 MATERIALS AND METHODS

3.2.1 Collection of Source Materials

Watershed materials were collected from various land use and land cover types in the watershed to develop a watershed spectral source library (WSSL). Soils and vegetation were sampled from the dominant land use categories in the Carters Creek basin. These categories were determined from the National Land Cover Dataset (NLCD), 2006, a Geographic Information System (GIS) data layer (Fig 3.1). Vegetation samples were collected from wetlands, scrub-shrub areas, urban parks, remnant forests, and homeowner lawns and commercial irrigated turfgrass strips around parking lots. Thirty five soil samples were sampled at 15cm depth directly below collected vegetation. Three soil cores within a 30 cm^2 area below the vegetation collected were collected at each sampling location and bulked. Soil samples were air dried and sieved through a 2mm sieve in preparation for extraction. Vegetation samples were oven dried 50° C then cut up in preparation for extraction.

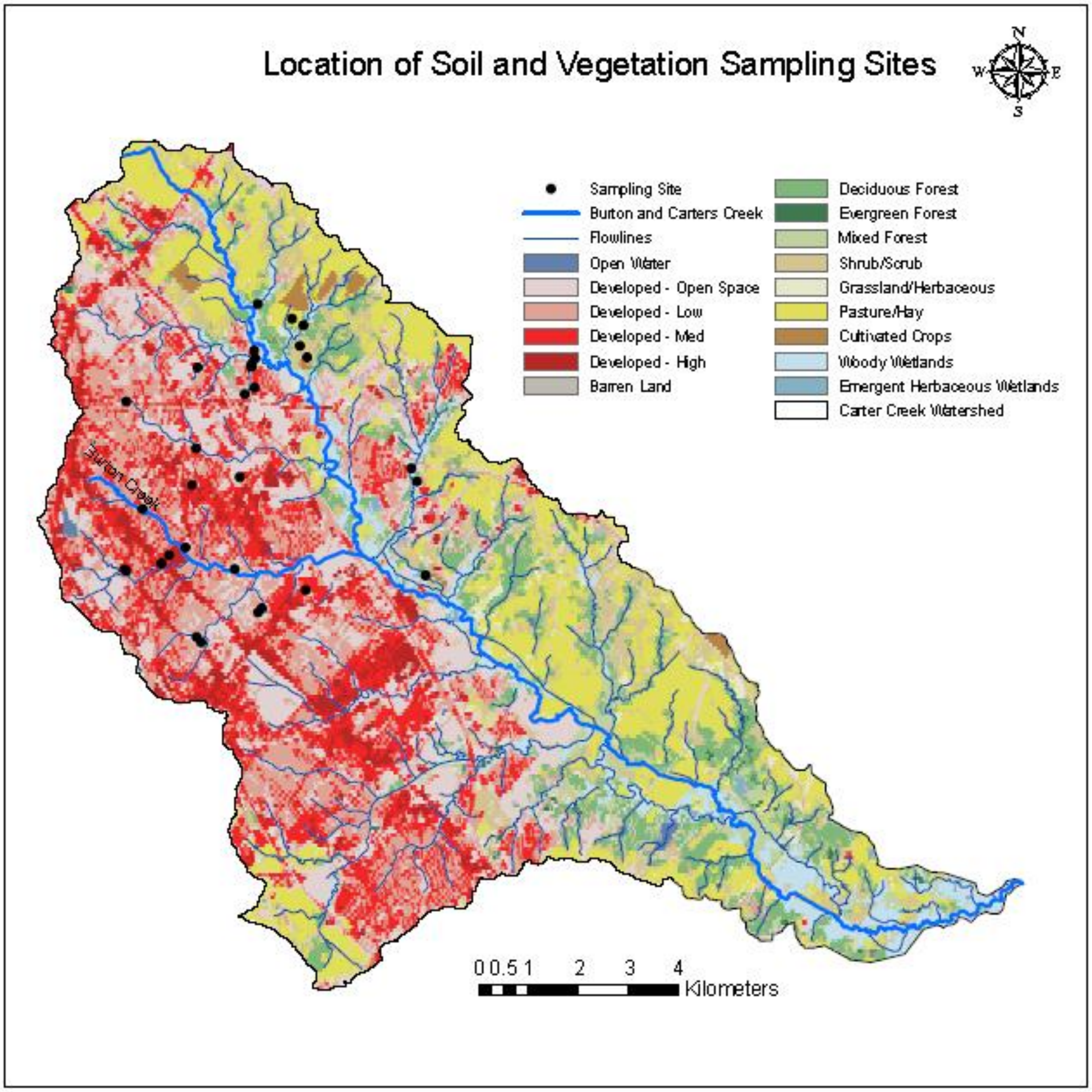


Fig. 3.1 Location of soil and vegetation sampling sites in the Carters Creek Watershed

A 1:10 ratio of soil:double distilled water (DDW) was placed into high-density polyethelene (HDPE) bottles and shaken at approximately 60 rpm for 1 hr before centrifugation at 15,000 rpm for 10 min (Sorvall RC6 Plus Centrifuge). Twenty mL of the supernatant was used for diffuse reflectance near infrared (DR-NIR) analysis. The remaining supernatant was filtered through Whatman GF/F (nominal pore size 0.7μm) filters and placed in 20mL HDPE bottles for other analyses not used in this study. For the extraction of vegetation I used a 1:40 ratio of vegetation:DDW with 1 hr shaking at approximately 60 rpm followed by centrifugation at 15,000 rpm for 10 min. Twenty mL of the vegetation supernatant was used for DR-NIR analysis.

Spectral signatures of some watershed materials collected for a previous study were also used in this study (Cioce 2012). These included fecal matter extracts from domesticated animals (chicken, cow, dog, racing pigeon) and wildlife (cliff swallow and feral hog). These were extracted using a 1:10 feces:DDW ratio and shaken for 1 hr at 60 rpm prior to centrifugation at 15,000 rpm for 10 min. Also collected and used for watershed source materials were samples from impervious surface runoff (rain and irrigation) with different traffic intensities and pavement substrate, sewage effluent from two wastewater treatment facilities, motor engine oil, and mammal decomposition products.

3.2.2 Collection of Stream Water

Stream water was collected monthly at 12 sampling locations over a one year period (July 2012-June 2013) as described in Chapter 2. Samples were collected upstream of bridges or in case of extremely low flow, directly from the channel in 500mL sterile whirl-pak bags. All samples were transported back to the lab within 4 hours of collection.

3.2.3 Diffuse Reflectance Near-Infrared (DR-NIR) Analysis

A simple evaporative technique was used to concentrate and isolate the organic compounds in the leached or extracted watershed source material and stream samples on a solid matrix was used (Aitkenhead-Peterson et al. in review). A 20mL unfiltered aliquot of source material extract or stream water was placed on white commercial sponges in a 500 mL Pyrex® beaker. After the sponge was saturated with the liquid sample, it was placed on a tinfoil tray and oven dried at 50° C for 48 h to ensure complete evaporation of the water prior to scanning the sponge.

A Labspec 5000 with wavelength ranges of 350 to 2500 nm at a 7nm resolution and provision of data at 1 nm intervals (Analytical Spectral Devices Inc., Boulder, CO, USA) was used in diffuse reflectance mode to gather spectral signatures of each of the extracted source materials and stream samples from each sponge. Three scans were taken from each sample sponge, rotating the sponge 90° between each scan. Three scans were also performed on a clean sponge as a baseline. A white Spectralite® disk was used to calibrate the instrument for 100% reflectance at the start of each analysis.

Pretreatment of the diffuse reflectance NIR (DR-NIR) data for the watershed source and stream materials included a 1st derivative transformation and then removal of the spectra obtained from the blank sponge from the sample sponge so that source material only was described. The three scans from the source materials or streams were then averaged. To remove noise either end of the spectra, data between 350 and 414 nm and 2441 and 2500 nm was removed from further analysis (Aitkenhead-Peterson et al. in review).

3.2.4 Modeling Watershed Sources

Principal Component Analysis (PCA) was applied to the WSSL to assess clustering of sources of organic material. This was followed by hierarchical cluster analysis (Euclidean distance using k-means clustering) on the WSSL data using 12 clusters with 100 iterations to minimize spatial outlier detection (SOD). However 15 clusters were used to sensibly separate known sources in the WSSL (Figure 3.2). Because it was expected that some of the watershed source spectra might change clusters because of their distance from other clusters, hierarchical cluster analysis was run ten times to confirm the groupings visualized during PCA. The resultant clusters are where source material fell into a cluster at least 70% (7 times out of 10) of the time.

Once the cluster analyses for the source material were completed, the spectral data for the watersheds were used in hierarchical cluster analysis with the WSSL. This analysis was also run ten times to assess the amount of times (%) that the stream sample fell within a certain cluster of watershed source materials. Most of the stream samples clustered with a watershed source cluster but approximately 10% of the stream samples fell between clusters indicating either a mixture of watershed sources or a source not yet identified.

Cluster analysis was performed 10 times for the combined WSSL and stream spectra and then the cluster data sorted so that each stream spectra fell into one cluster at least 20% (2 times out of 10) of the time.

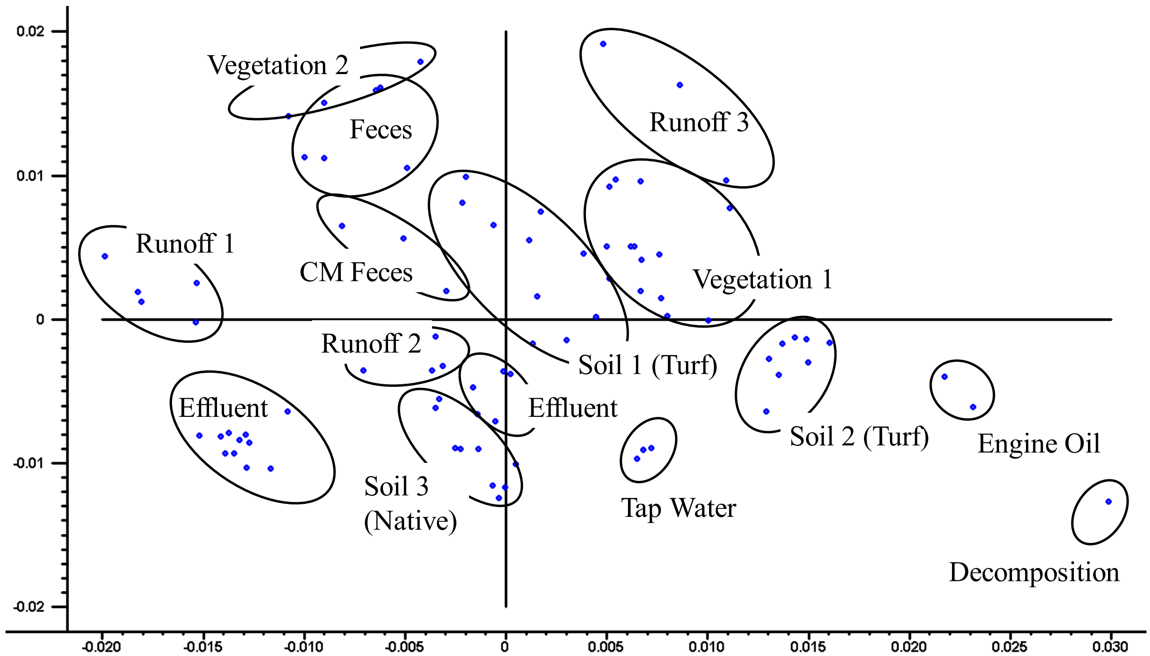


Fig. 3.2 Clustering of watershed source materials confirmed by hierarchical cluster analysis using Euclidean distance

3.3 RESULTS

3.3.1 Sources of Dissolved Organic Carbon to Streams

Stream water at Briar 2 had the same spectral signature as soil extract in July, August and December 2012 and March 2013 (Fig 3.3). Stream water at Briar 2 showed the same spectral signature as extracted turfgrass in September and October 2012 and February 2013. In April 2013 Briar 2 did not cluster with any group and so was allocated a mixed source.

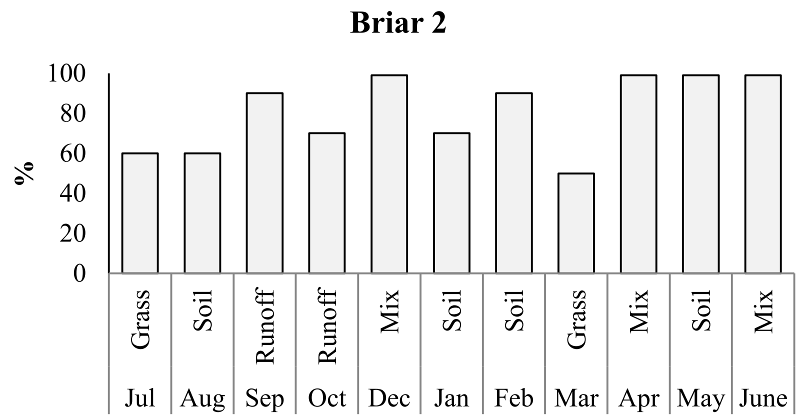


Fig. 3.3 Monthly sources of DOC to Briar 2 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Burton 1 (Fig 3.4) had the same spectral signature as extracted turfgrass in July, September and October 2012 and March 2013 and the same spectral signature as extracted soil in August, November and December 2012 and January 2013. In February 2013 the stream sample did not cluster with any group and was assigned a mixed source (Fig 3.4). In April 2013, 50% of the time the stream sample fell in the cluster containing Cliff Martin (CM) feces.

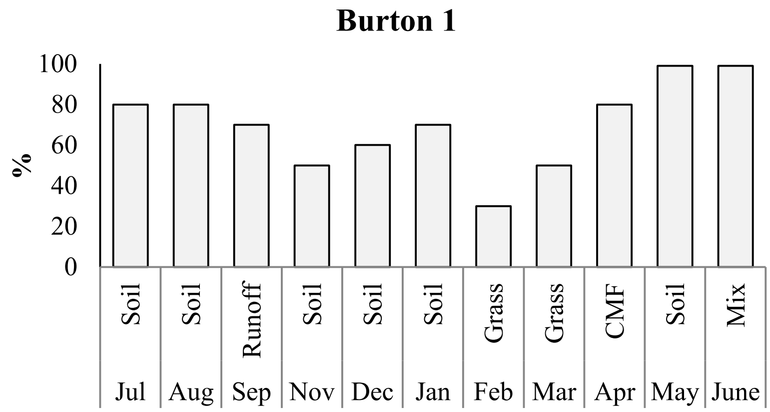


Fig. 3.4 Monthly sources of DOC to Burton 1 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Streamwater at Burton 2 had the same spectral signature as soil extract in August and November 2012 and May 2013 and the same spectral signature as turfgrass extract in July 2012 and March 2013. Runoff signatures were found in September 2012 and mixed signatures of indiscernible origin in April and June 2013 (Fig 3.5).

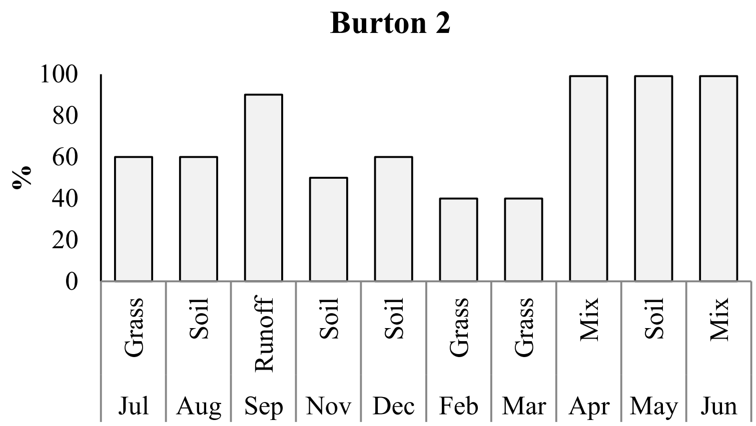


Fig. 3.5 Monthly sources of DOC to Burton 2 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Streamwater at Burton 3 had the same spectral signature as soil extract in July, August, November, and December 2012 and January, February, and May 2013 (Fig 3.6). Turfgrass extract spectral signatures were observed in March 2013 and runoff spectral signatures match with stream samples in September and October 2012. Spectral signatures in April and June 2013 did not have any distinguishable sources therefore a mixed source was allotted.

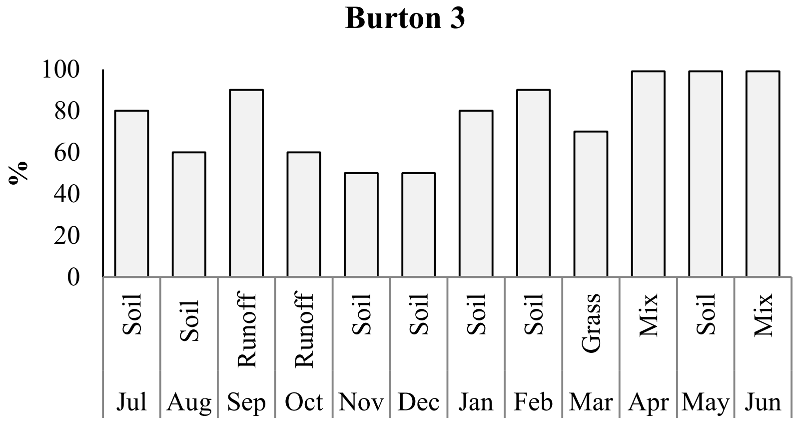


Fig. 3.6 Monthly sources of DOC to Burton 3 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Burton 4 had the same spectral signature as extracted turfgrass in March 2012 and soil extracts in July, August, and December 2012 and January, February, and May 2013 (Fig 3.7). In June 2013 the stream sample did not cluster with any group and was assigned a mixed source. In September, October, and November 2012, the stream sample fell in the cluster containing impervious surface runoff 70, 90, and 100% of the time respectively.

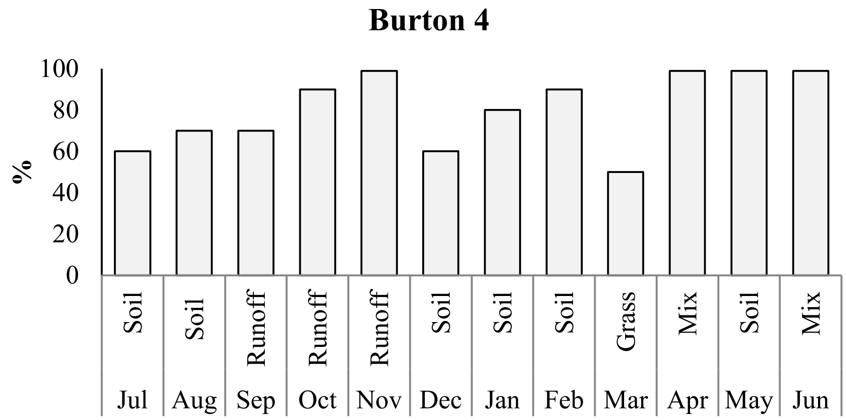


Fig. 3.7 Monthly sources of DOC to Burton 4 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Stream water at Burton 5 clustered with spectral signatures of urban soil extracts in July, November, December 2012 and February and May 2013 (Fig 3.8). Stream water was similar to spectral signatures of turfgrass extract in August 2012 and March 2013 and of impervious runoff in September 2012. In October 2012, April and June 2013, the stream sample did not cluster with any source and was assigned a mixed source.

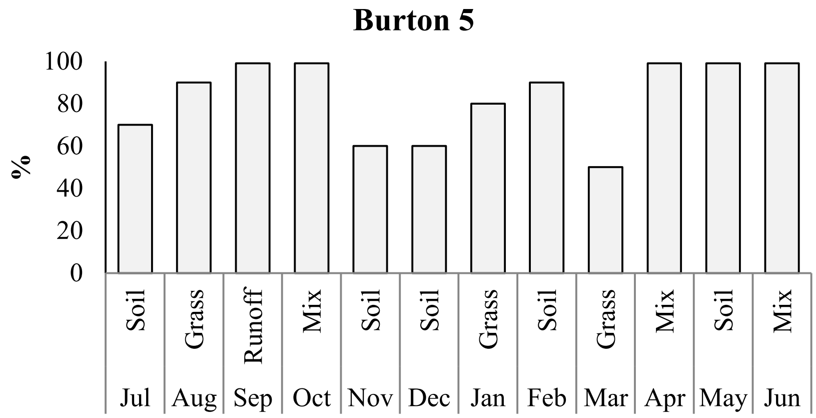


Fig. 3.8 Monthly sources of DOC to Burton 5 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Stream water at Carter 1 had the same spectral signatures as soil extract in July and December 2012, and in January 2013 (Fig 3.9). Turfgrass extract signatures only clustered with stream samples 30 and 50% of the time in February and March 2013. In May 2013 the stream sample did not cluster with any source, therefore a mixed source was designated. Stream water had the same spectral signatures as impervious runoff in October 2012 and June 2013.

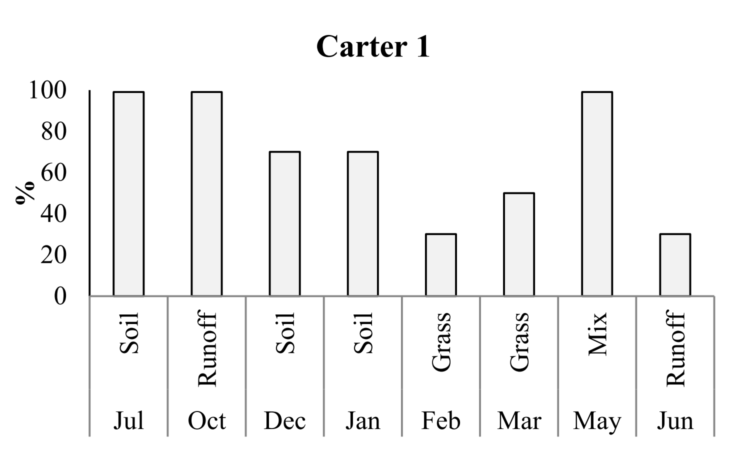


Fig. 3.9 Monthly sources of DOC to Carter 1 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Stream water at Carter 2 (Fig 3.10) had the same spectral signature as soil extract in August and November 2012 (Fig 3.10). In July 2012, February and March 2013 stream water clustered with soil turfgrass extracts, but only 80, 30, and 50% of the time respectively. In September 2012, the stream sample clustered with spectral signature of impervious runoff. No source could be determined in April 2013 as the sample did not cluster with any known source spectra.

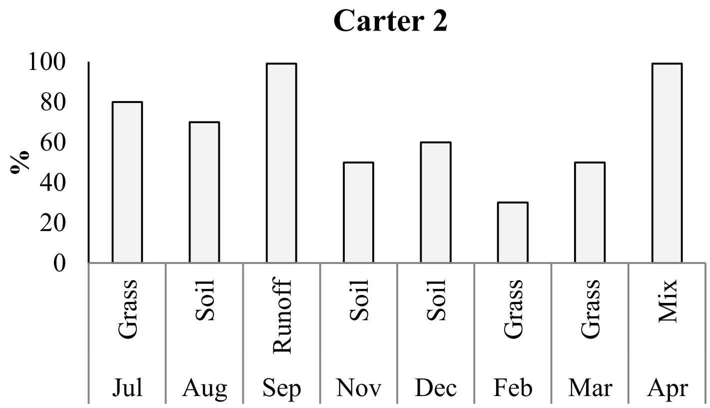


Fig. 3.10 Monthly sources of DOC to Carter 2 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Spectral signatures of stream samples from Carter 3 most closely aligned with turfgrass extracts and soil extracts (Fig 3.11). These relationships were found for turfgrass in July 2012, February and March 2013 for 80, 30, and 70% of the time respectively. Stream water samples clustered spectral signatures from urban soil extracts in August and December 2012, but only 60% of the time.

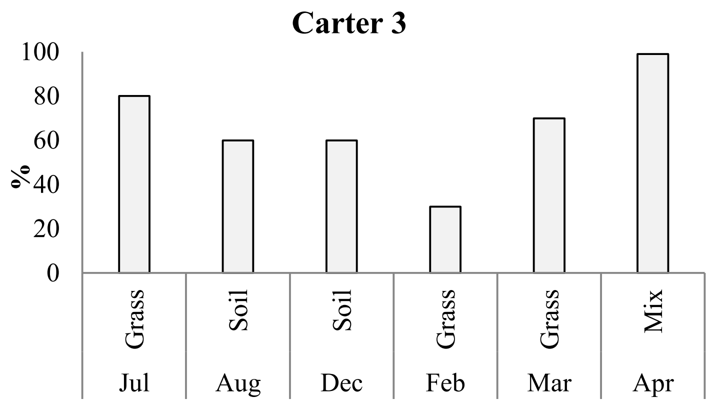


Fig. 3.11 Monthly sources of DOC to Carter 3 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Carter 4 clustered with extracted turfgrass in February and March 2013 for 30 and 50% of the time respectively. Spectral signatures of stream water clustered with urban soil extracts in July and December 2012 (Fig 3.12). In September and October 2012, Carter 4 stream samples clustered with impervious surface runoff. In April 2013 the stream sample did not cluster with any watershed source signature thus was assigned a mixed source.

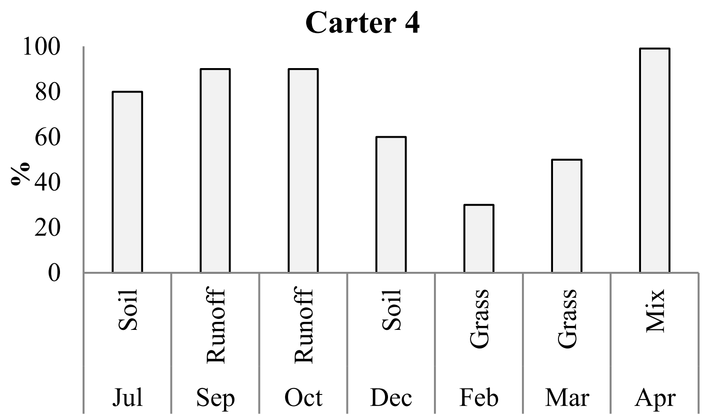


Fig. 3.12 Monthly sources of DOC to Carter 4 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Carter 5 stream samples clustered with extracted turfgrass in January, February and March 2013 for 60, 30 and 70% of the time respectively. Spectral signatures of stream water clustered with urban soil extracts in July-August 2012 and November-December 2013 (Fig 3.13). In September 2012 Carter 5 clustered with the spectral signature of impervious surface runoff. In April 2013 the stream sample did not cluster with any source spectral signatures and was assigned a mixed source.

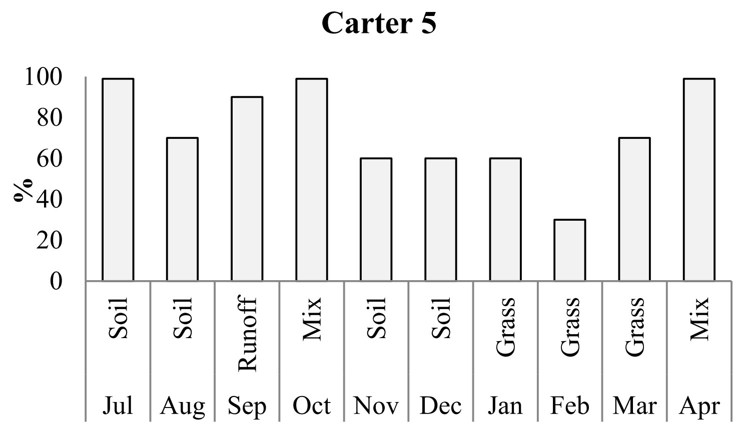


Fig. 3.13 Monthly sources of DOC to Carter 5 (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

Stream water at Country Club Branch clustered with soil extract in July and December 2012 (Fig 3.14). In February 2013 Country Club Branch stream water clustered with turfgrass extract. In April 2013 the stream sample did not align with any source, therefore a mixed source was designated.

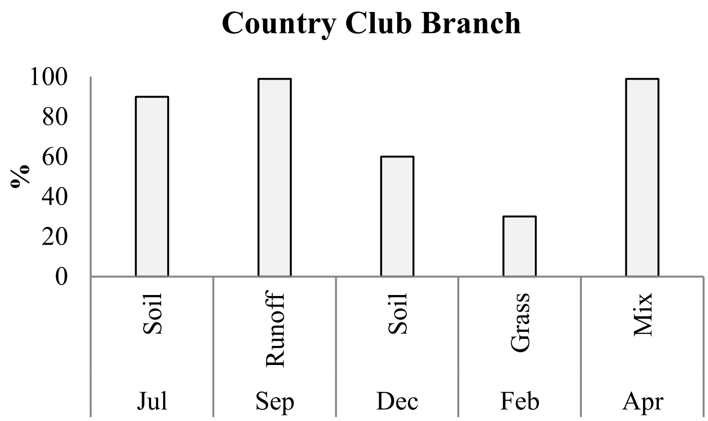


Fig. 3.14 Monthly sources of DOC to Country Club Branch (2012-2013). Percentages represent % time that cluster iterations of monthly stream samples clustered with specific watershed sources

3.3.2 Sources of Dissolved Organic Carbon at High versus Low Flow

To examine watershed sources of DOC during high and low flow events I described the percent of total sampling events for which specific source signatures clustered with stream water signatures during high and low flow (Figs 3.15 and 3.16). Spectral signatures at the Carter sites at high flow tended to cluster relatively strongly with that of turfgrass extract 50% of the time, except for Carter 1 and Carter 2 which clustered with extracted turfgrass signatures 70 and 40% of the time. Signatures of impervious urban runoff were observed at high flow at all sites except for Carter 1 and Carter 3 (Fig. 3.15). Country Club Branch was the only site for which sources could be assigned 100% of the time during high flow and no mixed sources were assumed.

Soil signatures represented greater than 50% of source signatures found in stream water at the Burton sites at high flow except for Briar 2 where it made up 40% of all sources (Fig 3.16). Turfgrass extract was the dominant source of DOC at all sites except

Burton 1, 3, and 4 for 17% of sampling events. Impervious urban runoff contributions were assigned to all Burton sites for 17% of total sampling dates at high flow and mixed sources to all except Burton 1 between 17-33% of the time. Burton 1 was the only stream for which Cliff Martin fecal matter spectral signatures were found in stream samples under any flow condition (Fig. 3.16).

Fewer watershed sources contributed to stream water DOC at low flow relative to high flow for 50% of the sites in the Carter Creek basin. The opposite was true for Carter 1, Carter 5, Burton 1, Burton 3, Burton 4, and Briar 2. Contribution from extracted turfgrass signatures was more prevalent in stream water at low flow than at high flow, ranging from 100% of sampling events at Country Club Branch and Carter 3 to 17% at Burton 4. Spectral signatures of soil extracts were found at most sites in the watershed at low flow except at Country Club Branch, Carter 3, and Carter 4. Soil was the dominant source at these sites from 20% of sampling events at Carter 1 and 5 to 50% of sampling events at Burton 3. Streams without runoff signatures at low flow included Country Club Branch, Carter 3, Carter 4, Burton 1, Burton 2, and Burton 5. No DOC contributions from fecal matter were found during low flow at any of the streams. Mixed source signatures were not dominant during any sampling events at low flow for the Carter sites; however were present at all the Burton sites.

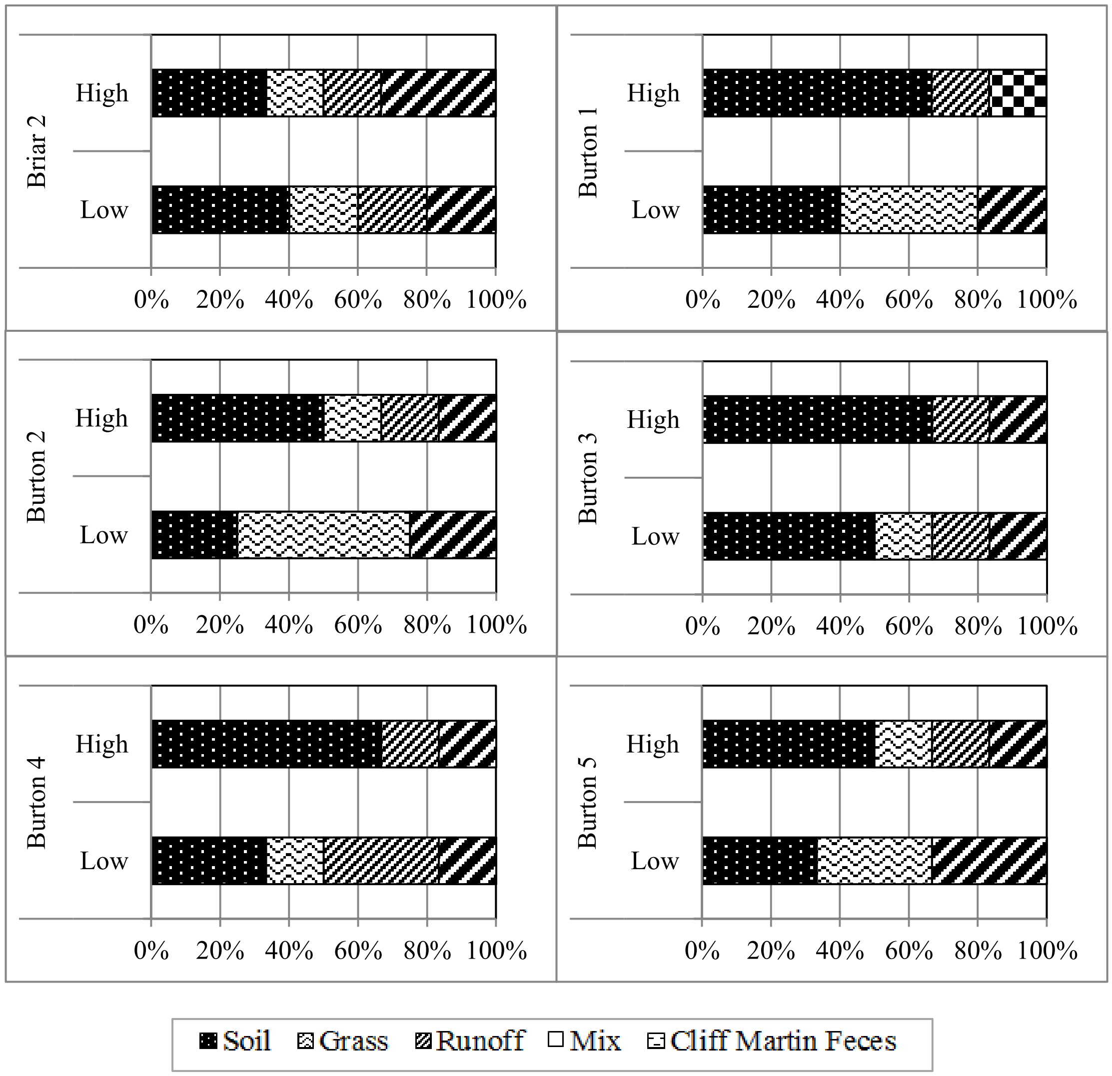


Fig. 3.15 Sources of streamwater DOC contributing to streams in the study under a) high and b) low flow conditions as percentage of total samples collected at the site in 2012-2013, for Carter 1-5, and CCB

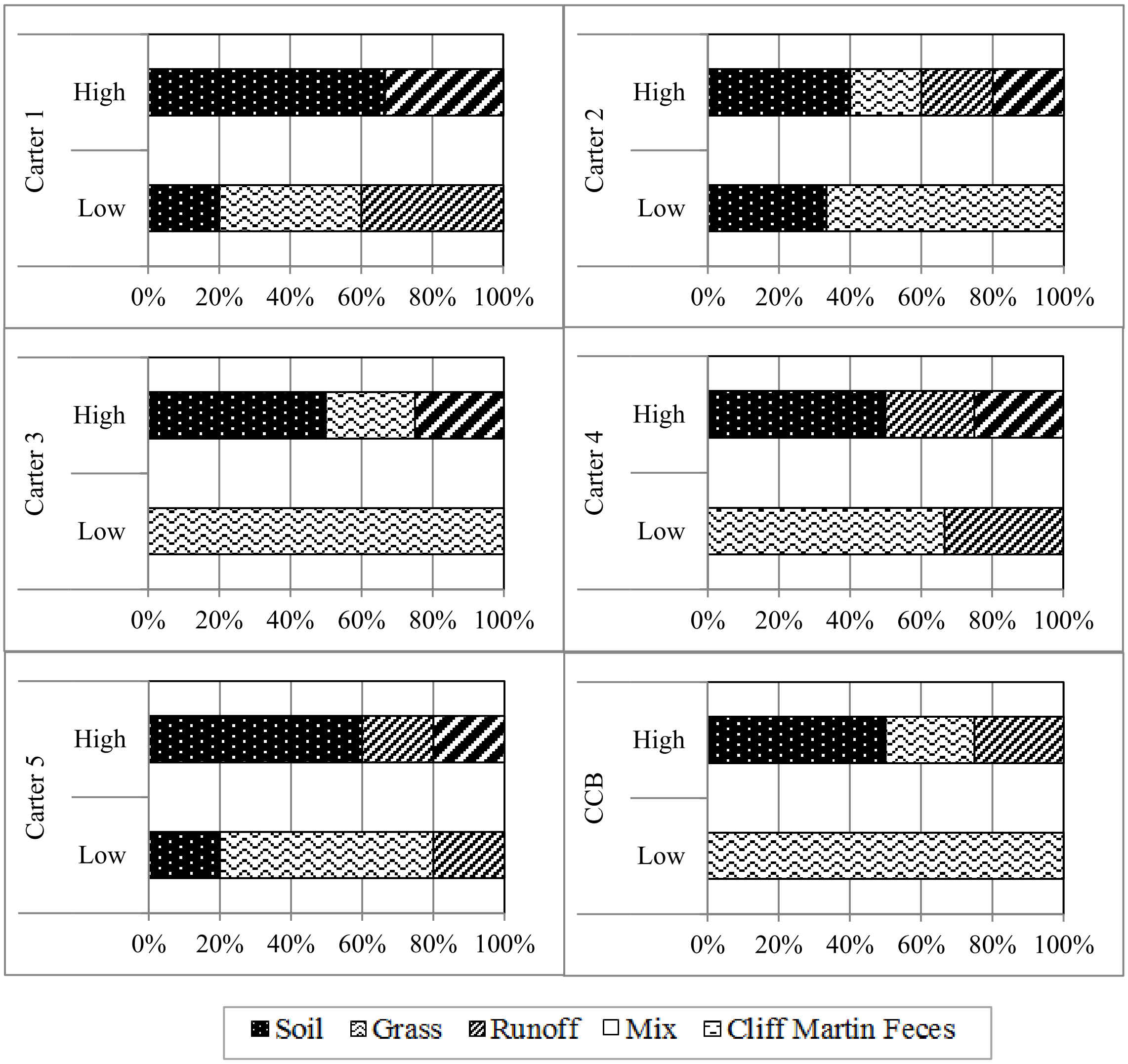


Fig. 3.16 Sources of streamwater DOC contributing to streams in the study under a) high and b) low flow conditions as percentage of total samples collected at the site in 2012-2013, for Burton 1-5, and Briar 2

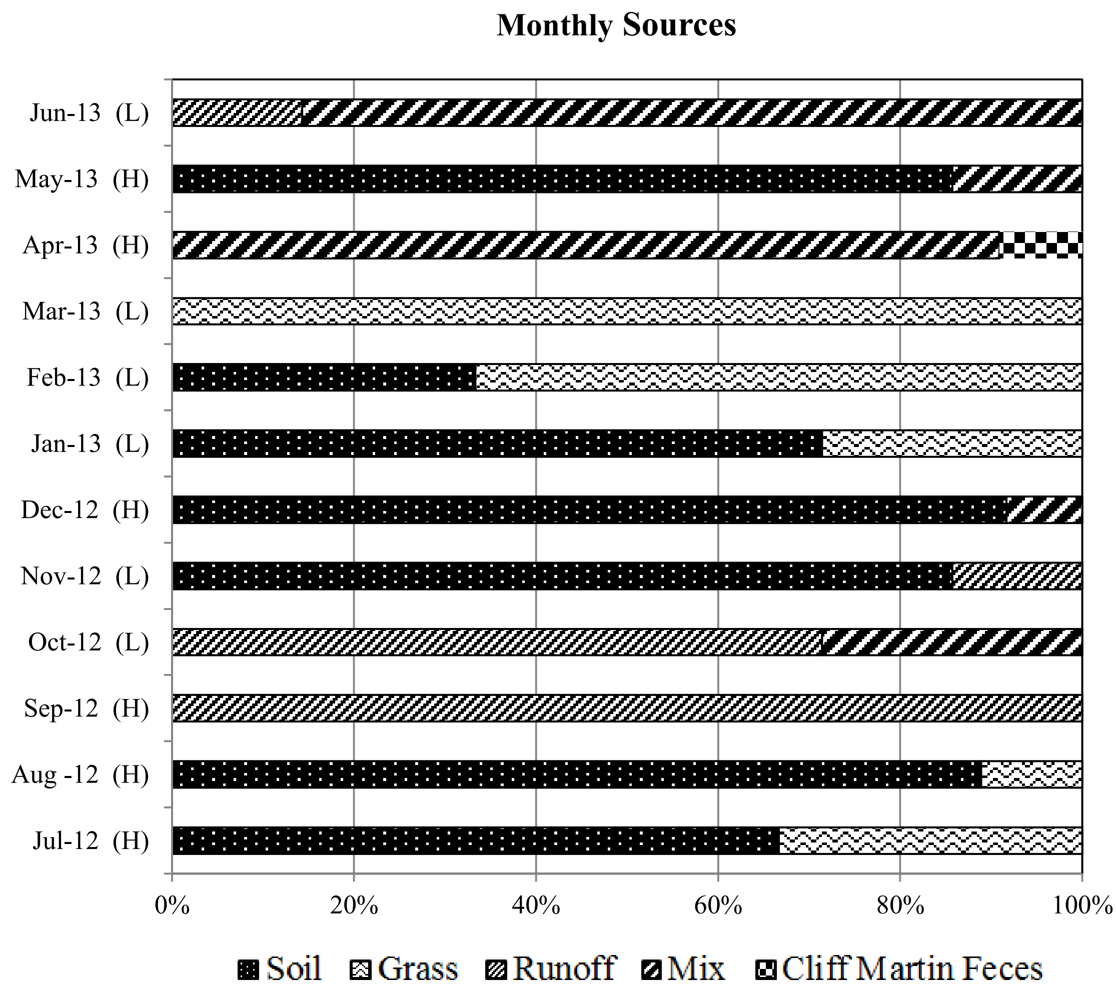
3.3.3 Monthly Sources of Dissolved Organic Carbon

DOC source origins in stream water were fairly consistent for all streams on a month to month basis. The majority of months had one or two dominant sources (Fig. 3.17), namely soil and turfgrass. In July, August, November, and December 2012 as well as

May 2013 stream water DOC prominently clustered with the spectral signatures of soil extracts. In February and March 2013 however, stream water samples clustered strongly to urban turfgrass extract spectral signatures. Urban impervious runoff signatures were prominent in stream spectra in September-October 2012 whereas a mixed source was found in July and April 2013.

3.4 DISCUSSION

Stream water DOC sources are influenced by an array of biological, chemical and physical watershed and climate characteristics. Catchment hydrology is especially known to strongly influence the transport of carbon to streams (Hope et al. 1994). Studies have found that stream water DOC is associated with hydrologic flow paths (Bishop et al. 1994), discharge (Hope et al. 1994; Inamdar et al. 2011), soil type or its characteristics (McDowell and Likens, 1988; Aitkenhead et al. 1999; Aitkenhead and McDowell 2000), and climate (Sickman et al. 2007). Disturbances to mechanisms which control these variables are therefore expected to affect subsequent streamwater DOC concentrations (Pitt et al. 2008) and their sources.



	Jul-12 (H)	Aug -12 (H)	Sep-12 (H)	Oct-12 (L)	Nov-12 (L)	Dec-12 (H)	Jan-13 (L)	Feb-13 (L)	Mar-13 (L)	Apr-13 (H)	May-13 (H)	Jun-13 (L)
Soil	8	8	0	0	6	11	5	4	0	0	6	0
Grass	4	1	0	0	0	0	2	8	11	0	0	0
Runoff	0	0	10	5	1	0	0	0	0	0	0	1
Mix	0	0	0	2	0	1	0	0	0	10	1	6
Feces	0	0	0	0	0	0	0	0	0	1	0	0
Total Samples	12	9	10	7	7	12	7	12	11	11	7	7

Fig. 3.17 Monthly sources of DOC to streams in the study as percent of total sites sampled that month. (H) = high flow, (L) = low flow

3.4.1 Discharge and Flowpaths

Discharge is a major predictor for transport of DOC to surface waters in natural landscapes (Hope et al. 1994; Aitkenhead-Peterson et al. 2007). During stormflow, riparian area and shallow groundwater from the vadose zone have been shown as primary contributors of DOC (Hinton et al. 1998; Katsuyama and Ohte 2002). Hinton et al. (1994) also found dominant contributions of DOC derived from shallow and deep groundwater, throughfall, and overland flow in rural catchments in central Ontario, Canada. Some studies have found more complex hydrologic patterns, suggesting that DOC is exported from multiple sources over the course of a single storm event (Inamdar et al. 2011) beginning with riparian groundwater at the start of an events followed by contributions from throughfall and leaf litter leachate attributed because of the increase in aromatic and humic substances, and finally soil water during the recession limb stage. This progression of sources likely occurs because storms flush DOC derived from catchment soils and plants by displacing concentrated pre-event waters from the vadose zone to the stream (Lafreniere and Sharp 2004). Since the concentrations of DOC in surface soil layers are typically higher than those in most mineral soils (Aitkenhead-Peterson et al. 2003), it is suggested that hydrologic flow paths may affect both spatial and temporal DOC exports to streams.

The proximity of watershed components to the stream may also play a role in the timing of DOC loadings. For example, near stream riparian area DOC contributions are identified in several studies as dominant additions to stream water (Bishop et al. 1994; Hinton et al. 1998; Inamdar et al. 2011), especially during storm events (Hook and

Yeakley 2005) and the first flush of water to the stream (Sickman et al. 2007). Overall, the source of streamwater DOC to the streams sampled in this study showed hydrological flowpaths through soil and turfgrass based on their clustering with watershed spectral signatures.

Urban soils are typically more compact than in undisturbed watersheds (Pitt et al. 2008). Hydrology of urban watersheds is significantly affected by this alteration of natural hydrologic flow paths (Sickman et al.2008). Hydrologic flowpaths in clay soils in particular are impacted by compaction (Pitt et al. 2008). Compaction reduces soil infiltration capacity and may cause increased incidence of Hortonion overland flow (Paul and Meyer 2001). This increased overland flow is more likely to have a mixed or more complex DOC signature than runoff seeping slowly through upper soil layers and turfgrass. Mixed sources were more commonly assigned to stream water in Burton Creek than at the Carter Creek sites in this study. Furthermore, a larger number of watershed source signatures were found in the Carter Creek sites. This is logical given the fact that Burton Creek watersheds are more urbanized and I assume have greater soil compaction than the more rural headwaters of Carters Creek. Loss of soil organic matter from urban soils as a result of soil disruption is believed to enhance streamwater DOC (Sickman et al. 2007). This may explain why soil spectral signatures were observed more commonly at the urban Burton Creek sites compared to the rural Carter Creek Sites during all flow conditions. In addition to this, the effect of antecedent soil moisture conditions (Table 2.3) on runoff from soils is likely more prominent in rural areas with lesser impervious surfaces (Pitt et al. 2008). This may also explain why soil signatures were seen at the

Burton Sites more frequently than at the Carter sites, especially during low flow. Runoff from irrigation in urban areas during the dryer months would maintain soil signatures observed at low flow however rural areas lacking this irrigation wouldn't have such strong soil signatures in streams during low flow. Along similar lines, antecedent moisture conditions are also a possible explanation of source patterns observed in August 2012 and in February 2013. In August 2012, soil extract signatures dominated at 89% of the stream sites sampled, whereas in February 2013 turfgrass extract spectral signatures were dominant at almost 70% of the stream sample sites (Fig 3.17). In-situ decomposition of organic matter in the wintertime probably yielded similar signatures as compared to live vegetation. Furthermore continuous rainfall in the 72h prior to the sampling event in August (Table 2.3) likely supplied sufficient precipitation to infiltrate soils thoroughly and flush out previously present subsurface shallow soil water. In February however low antecedent soil moisture conditions probably meant greater retention of soil water from the precipitation event, lesser flushing of soil water and a subsequent increase in vegetation signatures in stream water.

The intensity and duration of storm events can play a role in source contributions. Quick storm events depositing a lot of rain in a short period of time do not allow enough time for water to infiltrate soil thus reducing water residence in the soil (Inamdar et al. 2011) and flush out previously accumulated soil water high in DOC (Lafreniere and Sharp 2004). A high intensity, short duration rain event in September 2012 resulted in a greater contribution of impervious surface runoff to streams relative to soil based on stream clustering with watershed spectral signatures. Whereas long duration, low intensity storm events, observed in May and December 2013 produce soil spectral signatures in stream water. Some stream water spectra during low flow also clustered with impervious runoff. For example in October 2012, when there was no rainfall accumulation 72h prior to the sampling event there was evidence of impervious runoff based on stream samples clustering with runoff spectra. Commercial enterprises and homeowners are still irrigating their landscapes in October and for the most part irrigating to runoff from their property. Over irrigation resulting in runoff and onto impervious surfaces is a common observation in the region. These results indicate that temporal variability of precipitation effects in conjunction with antecedent moisture conditions can effect relative source contributions to the stream.

3.4.2 Other Contributing Factors

3.4.2.1 Seasonality

Flow conditions alone do not dictate relative source contribution of DOC to streams. Such contributions from both surficial and groundwater sources are closely linked with climate and seasonality. This argument is supported by a study in the Bow River watershed, Canada which found that seasonal flow routing of runoff affected DOC composition and concentration (Lafreniere and Sharp 2004). The amount of water contact time with organic soils and litter was found to shift DOC fluorescence signatures indicating that soil and plant organic matter was the primary source of summer DOC in streams. Shallow subsurface flow was alluded to as the mechanism contributing to this pattern. Similarly Inamdar et al. (2011) demonstrated runoff from storm events in the summertime had largest contributions from surficial watershed sources. No seasonal variability in DOC sources was identifiable at any of the sites in this study. This may be due to the lack of four seasons and the supplemental irrigation applied to urban landscapes typically from March until November.

The Inamdar et al. (2011) was conducted in forested watersheds in the mid-Atlantic region which would depend upon rain events to move DOC off the landscape. My study was conducted in urban and rural watersheds where irrigation of homeowner and commercial landscapes and some city parks occurs between March and November. Most irrigate enough to generate runoff onto surrounding impervious surfaces which flow into storm drains directly to streams.

Algal contributions in the summer time may also have added DOC to stream water at my sites. Although all streams which had stagnant (no observable flow) water collected and high algal density were removed from analysis, some flowing streams had aquatic plants and algal patches. In June 2013 most streams displayed mixed sources at low flow conditions. Field observations showed aquatic vegetation and algae was present in all streams. A study by Kaplan and Bott (1982) in a Piedmont stream showed that algal DOC contributions comprised up to 20% of total DOC export in the watershed. Thus, leached DOC from aquatic plants and algae could be an unaccounted for DOC source in the WSSL. Steele and Aitkenhead-Peterson (2013) reported that as stream water sodium adsorption ratio (SAR) increased so did the contribution of leached DOC from allochthonous sources such as leaf litter and lawn clippings transported to streams; the SAR of streams could have a similar effect on leaching DOC from aquatic plants and algae. Inversely, Wetzel (2003) suggested that observed heterotrophic biotic productivity of most lakes and rivers could not possibly be supported by autochthonous sources of DOC and must be supplemented by allochthonous sources imported from terrestrial and the land-water interface regions. The contribution of aquatic photosynthetic organisms and bacteria, phytoplankton, and macrophytes, to stream water DOC (autochthonous sources) can be expected in some surface waters such as lakes and stagnant or slow flowing rivers (Keeley and Sandquist 1992). In lentic waters, δ13 C values of freshwater aquatic material vary from -11 to -50‰ (Keeley and Sandquist 1992). In streams in the Bryan/College Station region during times of low flow, there was some evidence of *Lemna gibba* (duckweed), which has a δ13 C of -29.8 to -28.5‰ in Oregon streams (Bonn and Rounds 2010) but that does not correspond to δ13 C signatures of Bryan/College Station surface waters which ranged from -27 to -21 ‰ (Cioce et al. in review). In Oregon streams Bonn and Rounds (2010) suggested that leakage of carbon from duckweed was not considered a major contributor to DOC. However, to test this theory further, aquatic plants and algal spectral signatures need to be collected and added to the WSSL.

Urban organic matter sources such as partially decomposed vegetation that accumulated on catchment surfaces in dry summers are washed into urban streams during storm events (Sickman et al. 2007). I did not observe frequent vegetation signatures in the urban streams in my study during high flow. However, no forest leaf litter or materials from shrub scrub vegetation were included in the WSSL I constructed and it is possible that these sources also contributed to my mixed source categories. This is a possible reason why urban vegetation signatures were not more prominent at the

Burton sites during high flow. The buildup up and subsequent flushing of organic matter from impervious surfaces is a process unique to urban areas. It may explain why mixed sources were commonly found at Burton sites than in the Carter Creek headwaters.

3.4.2.2 Waste Water Treatment Plant

High nutrients such as nitrate-N and orthophosphate-P are typically observed downstream from waste water treatment facilities (Chapter 2). I did not however observe a signature of sewage effluent in Carter 5 which is sampled downstream of a WWTF. This makes some sense as much of the DOC is removed to lower the carbonaceous oxygen demand during the secondary treatment process. Thus the DOC in Carter 5 is derived either from the watershed soil, turfgrass or impervious runoff (allochthonous sources) depending upon its hydrological flowpath to the stream. This finding supports the findings of McCrary et al. (2013) who stated that recovery and regrowth of *E. coli* was due to nitrogen and phosphorus derived from sewage effluent and DOC derived from the watershed as runoff. On the contrary, Westerhoff and Anning (2000) found that DOC in effluent-dependent streams to be characteristic of autochthonous sources (microbial origin) which would be consistent with microbial metabolites released during the secondary treatment process. It is likely that due to the low concentrations of DOC in effluent (McCrary et al. 2013) relative to urban streams in the region (Aitkenhead-Peterson et al. 2009; Harclerode et al. 2013) that the signature of effluent was perhaps overwhelmed by vegetation and soil sources.

3.4.3 Tracking Watershed Sources of DOC Using DR-NIR Spectroscopy

Testing the use of diffuse reflectance near-infrared spectroscopy (DR-NIRS) with a WSSL to source track stream DOC indicated that DR-NIR can be a relatively fast and cost effective technique to determine terrestrial sources of DOC to streams. Using this methodology in my study, I found similar results as reported in other studies (Lafreniere and Sharp 2004; Inamdar et al. 2011) with the majority of watershed source signatures derived from surficial watershed sources such as soil and vegetation. The commercial sponges used are an inexpensive ($0.10 each) and readily available medium for conducting watershed source tracking.

The largest limitation to the WSSL approach for tracking relative source contributions of DOC to surface waters is the size and variability of the spectral library. In my study, signatures of algae, coarse woody debris, riparian soil and vegetation, and forest leaf litter, shrub, scrub and pasture vegetation were not included. I had made the assumption that soil and vegetation collected in an earlier study (Cioce 2012) for producing a regional watershed WSSL which included forest, shrub-scrub and pasture vegetation and soil could be used to assign watershed sources to my streams. However, the turfgrass vegetation and soils collected during 2010-2011 (Cioce 2012) did not cluster well with the turfgrass vegetation and soils I collected in 2012-2013 suggesting an annual variation occurs in extract signatures. Furthermore, stream water signatures in this study did not cluster with older soil and vegetation data collected at all but clustered instead with the soil and vegetation collected and extracted during the stream sampling period. This suggests that a long-term WSSL is not feasible for soil and vegetation signatures to be observed in streams at a later date. However, spectral signatures from impervious runoff from rain events or over irrigation did not change between 2010 and 2013. Aside from these limitations in the WSSL design, the number of sampling events is another limitation to the study. In small headwater streams where stagnant water or very low flow is common, samples are difficult to collect. In this study analysis was conducted using only samples collected from flowing streams which limited our number of samples from some of my streams. However, given research indicating the influence of autochthonous sources on stream water DOC concentrations, future work investigating DOC sources during low flow conditions is recommended.

3.5 CONCLUSIONS

DOC concentrations in surface waters are complex and influenced by multiple factors. Source contributions may be affected by mechanisms which alter hydrologic processes controlling DOC dynamics. Other variables including soil disturbance, antecedent soil moisture conditions, intensity of storm events and seasonality are also important factors to consider. The major sources of DOC into the Carter Creek basin watersheds were leachate from soil and turfgrass. Turfgrass signatures seen in the rural headwaters of Carters Creek may derive from meadows with similar vegetation signatures. Aquatic vegetation may account for some DOC contributions, but this needs to be tested.

CHAPTER IV

SUMMARY

In recent years a paradigm shift from targeting point source pollution to a focus on non-point source pollution has become popularly advertised by the EPA (EPA 2013). A watershed approach, using a systems theory, where all ecosystem components are considered in planning efforts is now preferred to target best management practices. Understanding the relationships between watershed components and their association to water chemistry at various scales is essential in identifying nutrient exports. With the added complexity of disturbance that human activities bring to watersheds and further, the interruption of natural watershed-surface water dynamics it becomes clear that managing non-point source pollution is no easy task. In my study, I utilized a standard and novel ideology to identify sources of nutrient and carbon pollution to surface waters and discuss the mechanisms behind them.

Urbanization has been documented in many studies to impact nutrient and carbon dynamics on a watershed scale. My research showed that higher nutrient and carbon concentrations are present in the Carters Creek watersheds compared to 2007. This finding supports the results of many studies who claim higher concentrations in urban watersheds compared to rural watersheds is likely a result of human activities. Multiple variables play a role in this. The most important of these variables are hydrologic flow paths which are key to understanding the dynamics that lead to these results, especially in disturbed watersheds. Surface water originating from rainfall or irrigation travels over and through watershed surfaces, picking up traces of signatures from soil, vegetation, and any pollutants on urbanized surfaces such as fecal matter, rubber by-products from tires, or engine oil. Identifying problem areas contributing to these problems can assist in efficient implementation of mitigation strategies.

The ability to identify problem areas has two primary benefits. Firstly, it narrows down scope for establishment of best management practices to mitigate problematic non-point source pollution. Secondly, enables watershed managers to 'hone in' on possible mechanisms which may result in higher terrestrial nutrient and carbon export to surface waters. A nested watershed approach as used in Chapter II, to examining surface water quality allows for this. Alternatively, recently emerging chemometric methods, such as the use of DR-NIRS to extract chemical signatures in watershed sources and cluster them with stream water samples such as in Chapter III, potentially enables greater and more detailed source identification. This technique is more cost-effective and source specific than current identification methods. A watershed spectral source library (WSSL) methodology is useful for fine scale identification of local sources of carbon. Further temporal analysis can supplement this technique to spatially and seasonally understand watershed carbon dynamics. The technique however is limited by the size of the WSSL. It must be adapted to suspected local carbon sources and expanded in size for greater analytical power.

In conclusion, urban water quality dynamics are extremely complex. Nutrient and carbon cycles are coupled with physical, biological, and chemical landscape parameters. Altering one affects the other. Therefore, identifying the underlying mechanisms resulting in elevated nutrient and carbon dynamics and their spatial distribution can aid development of long term solutions to controlling both non-point source and point source pollution in urbanizing watersheds.

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APPENDIX A

MONTHLY WATER CHEMISTRY DATA FOR STREAM SAMPLES COLLECTED BETWEEN JULY 2012 AND JUNE 2013 WITHOUT STAGNANT SAMPLES

Date	Name	Flow	ID	pH	EC	NO_3-N	NH_4-N	PO_4-P	DOC	TN	DON
					µS cm^{-1}	mg L^{-1}					
10/21/2012	Briar 2	low	5690	8.24	365	1.21	0.23	0.31	41.39	1.75	0.31
1/27/2013	Briar 2	low	5767	8.75	395	0.17	0.23	0.20	40.08	1.00	0.61
2/22/2013	Briar 2	low	5779	7.79	530	0.19	0.24	0.16	39.25	0.85	0.42
3/29/2013	Briar 2	low	5871	7.99	430	0.18	0.27	0.19	42.30	1.07	0.62
6/17/2013	Briar 2	low	5941	8.10	450	0.24	0.23	0.28	14.47	1.07	0.60
7/13/2012	Briar 2	high	5604	7.66	240	0.13	0.31	0.26	35.22	1.16	0.73
8/20/2012	Briar 2	high	5649	7.9	255	0.27	0.23	0.23	36.35	1.33	0.83
9/17/2012	Briar 2	high	5660	7.69	570	0.26	0.21	0.21	58.07	1.49	1.02
12/10/2012	Briar 2	high	5741	7.59	215	0.52	0.22	0.22	28.86	1.00	0.27
4/21/2013	Briar 2	high	5845	7.77	380	0.19	0.30	0.22	46.23	1.34	0.85
5/22/2013	Briar 2	high	5915	7.67	175	0.32	0.32	0.64	19.17	2.60	1.96
10/21/2012	Burton 1	low	5680	9.25	500	0.10	0.25	0.18	43.50	1.24	0.89
11/25/2012	Burton 1	low	5725	8.81	780	0.76	0.20	0.27	36.82	1.73	0.77
1/27/2013	Burton 1	low	5762	8.42	1015	0.79	0.23	0.19	74.01	1.87	0.86
2/22/2013	Burton 1	low	5774	9.17	730	0.94	0.21	0.18	41.78	1.46	0.31
3/29/2013	Burton 1	low	5852	8.62	660	0.93	0.20	0.24	52.55	1.51	0.37
7/13/2012	Burton 1	high	5601	8.2	340	0.29	0.20	0.17	27.09	1.18	0.69
7/25/2012	Burton 1	high	5610	9.38	1080	0.20	0.29	0.09	92.39	3.44	2.95
8/20/2012	Burton 1	high	5639	7.33	365	0.11	0.22	0.27	57.86	2.05	1.72
9/17/2012	Burton 1	high	5655	7.72	220	0.19	0.22	0.11	34.15	0.97	0.57

12/10/2012	Burton 1	high	5736	7.82	420	0.78	0.23	0.25	42.40	1.53	0.52
4/21/2013	Burton 1	high	5840	8.66	400	0.18	0.23	0.32	46.99	1.09	0.69
5/22/2013	Burton 1	high	5910	7.87	190	0.31	0.31	0.37	0.59	0.68	0.06
11/25/2012	Burton 2	low	5726	9.06	1360	0.08	0.20	0.15	48.49	1.66	1.38
2/22/2013	Burton 2	low	5775	10	580	0.10	0.22	0.04	41.42	1.07	0.74
3/29/2013	Burton 2	low	5853	9.3	1420	0.10	0.22	4.89	93.33	1.71	1.39
6/17/2013	Burton 2	low	5937	9.20	1250	0.20	0.17	0.10	20.33	1.21	0.84
7/13/2012	Burton 2	high	5600	8.89	270	0.18	0.21	0.17	26.60	1.12	0.73
8/20/2012	Burton 2	high	5640	10.34	750	0.08	0.22	0.09	73.07	3.65	3.34
9/17/2012	Burton 2	high	5656	7.95	410	0.35	0.20	0.13	54.54	1.81	1.26
12/10/2012	Burton 2	high	5737	8.51	390	0.19	0.20	0.20	45.72	0.86	0.46
4/21/2013	Burton 2	high	5841	10.08	765	0.17	0.20	0.17	96.32	2.58	2.21
5/22/2013	Burton 2	high	5911	8.15	185	0.34	0.34	0.37	13.95	2.14	1.47
10/21/2012	Burton 3	low	5682	8.42	1205	0.15	0.22	0.14	73.66	1.16	0.80
11/25/2012	Burton 3	low	5727	8.13	1015	0.13	0.19	0.15	83.73	0.58	0.26
1/27/2013	Burton 3	low	5764	8.06	1165	0.10	0.23	0.09	57.79	0.97	0.64
2/22/2013	Burton 3	low	5776	8.46	770	0.09	0.21	0.05	11.24	0.42	0.12
3/29/2013	Burton 3	low	5854	8.16	1230	0.11	0.19	0.22	57.74	0.80	0.51
6/17/2013	Burton 3	low	5938	8.45	1080	0.33	0.22	0.19	16.62	1.04	0.49
7/13/2012	Burton 3	high	5602	7.85	650	0.31	0.21	0.08	33.93	1.04	0.52
7/25/2012	Burton 3	high	5612	8.6	820	0.27	0.20	0.28	17.38	0.71	0.23
8/20/2012	Burton 3	high	5641	8.09	365	0.12	0.23	0.21	39.92	1.00	0.65
9/17/2012	Burton 3	high	5657	7.71	590	0.14	0.29	0.20	78.51	2.64	2.21
12/10/2012	Burton 3	high	5738	8.24	380	0.23	0.20	0.21	46.55	0.95	0.52
4/21/2013	Burton 3	high	5842	8.42	635	0.20	0.20	0.56	48.65	0.82	0.42
5/22/2013	Burton 3	high	5912	8.01	300	0.22	0.22	0.40	22.19	2.38	1.95
10/21/2012	Burton 4	low	5683	10.43	730	0.09	0.21	0.20	64.13	1.69	1.39
11/25/2012	Burton 4	low	5728	9.24	1700	0.11	0.22	0.13	197.15	3.19	2.86
1/27/2013	Burton 4	low	5765	9.96	545	0.13	0.23	0.18	48.36	1.03	0.66

2/22/2013	Burton 4	low	5777	9.27	500	0.07	0.22	0.10	23.71	0.68	0.39
3/29/2013	Burton 4	low	5855	8.21	460	0.11	0.22	0.44	59.20	1.31	0.98
6/17/2013	Burton 4	low	5939	9.30	1505	0.21	0.19	0.16	16.16	1.28	0.88
7/13/2012	Burton 4	high	5598	7.82	425	0.28	0.22	0.20	18.69	1.22	0.72
8/20/2012	Burton 4	high	5642	7.96	320	0.25	0.24	0.32	51.04	2.40	1.91
9/17/2012	Burton 4	high	5658	8.15	540	0.14	0.42	0.13	65.50	2.28	1.73
12/10/2012	Burton 4	high	5739	7.91	290	0.50	0.21	0.44	32.83	1.46	0.75
4/21/2013	Burton 4	high	5843	9.4	260	0.16	0.21	0.26	36.22	1.18	0.81
5/22/2013	Burton 4	high	5913	7.91	205	0.29	0.29	0.51	20.04	2.44	1.87
10/21/2012	Burton 5	low	5684	8.52	600	0.22	0.20	0.24	40.47	0.92	0.50
11/25/2012	Burton 5	low	5729	8.51	1070	0.08	0.20	0.20	28.38	0.72	0.45
1/27/2013	Burton 5	low	5766	8.26	860	0.09	0.23	0.24	34.28	1.30	0.98
2/22/2013	Burton 5	low	5778	8.12	705	0.22	0.20	0.07	40.67	0.67	0.25
3/29/2013	Burton 5	low	5870	8.33	790	0.13	0.21	0.19	75.02	1.76	1.42
6/17/2013	Burton 5	low	5940	8.24	1100	0.20	0.18	0.06	42.92	2.22	1.84
7/13/2012	Burton 5	high	5599	7.8	260	0.39	0.24	0.18	22.24	1.11	0.49
7/25/2012	Burton 5	high	5614	7.9	870	0.19	0.31	0.27	39.61	1.40	0.89
8/20/2012	Burton 5	high	5643	8.02	610	0.16	0.29	0.34	63.38	4.16	3.71
9/17/2012	Burton 5	high	5659	8.15	675	3.74	0.21	0.83	73.60	5.86	1.91
12/10/2012	Burton 5	high	5740	7.96	390	0.17	0.27	0.19	27.66	1.08	0.64
4/21/2013	Burton 5	high	5844	7.91	420	0.67	0.27	0.35	44.84	1.73	0.79
5/22/2013	Burton 5	high	5914	7.99	170	0.43	0.43	0.36	12.15	2.24	1.37
10/21/2012	Carter 1	low	5685	7.43	320	0.46	0.23	0.21	51.66	1.83	1.15
1/27/2013	Carter 1	low	5757	8.15	240	0.47	0.24	0.07	38.75	2.32	1.61
2/22/2013	Carter 1	low	5769	7.16	220	0.16	0.26	0.05	29.51	1.00	0.59
3/29/2013	Carter 1	low	5847	7.08	190	0.11	0.20	0.04	36.35	1.34	1.03
6/17/2013	Carter 1	low	5931	8.81	310	0.19	0.17	0.11	20.70	1.18	0.83
7/13/2012	Carter 1	high	5605	7.45	140	0.22	0.26	0.14	14.32	0.84	0.36

12/10/2012	Carter 1	high	5731	6.82	150	0.90	0.37	0.39	24.28	1.99	0.72
5/22/2013	Carter 1	high	5905	8.79	70	0.30	0.30	0.19	17.07	2.02	1.43
11/25/2012	Carter 2	low	5722	7.89	555	0.08	0.21	0.18	66.20	1.21	0.92
2/22/2013	Carter 2	low	5770	8.51	400	0.16	0.20	0.09	33.65	0.72	0.37
3/29/2013	Carter 2	low	5848	8.83	520	0.12	0.21	0.04	52.32	1.31	0.97
6/17/2013	Carter 2	low	5932	8.22	460	0.19	0.18	0.25	14.50	1.14	0.76
7/13/2012	Carter 2	high	5606	8.06	390	0.32	0.27	0.19	48.31	1.74	1.16
8/20/2012	Carter 2	high	5645	7.74	360	0.20	0.31	0.14	39.41	1.42	0.91
9/17/2012	Carter 2	high	5651	7.32	460	0.16	0.20	0.17	59.29	1.56	1.21
12/10/2012	Carter 2	high	5732	7.68	215	0.59	0.20	0.22	22.81	1.06	0.27
4/21/2013	Carter 2	high	5836	7.56	360	0.22	0.25	0.11	47.25	0.98	0.51
5/22/2013	Carter 2	high	5906	8.26	155	0.30	0.30	0.28	16.01	2.19	1.59
2/22/2013	Carter 3	low	5771	8.31	370	0.16	0.20	0.06	14.43	0.63	0.27
3/29/2013	Carter 3	low	5849	8.47	330	0.13	0.21	0.12	39.08	0.80	0.46
6/17/2013	Carter 3	low	5933	8.35	300	0.20	0.22	0.15	15.77	1.12	0.70
7/13/2012	Carter 3	high	5607	7.58	310	0.10	0.22	0.11	19.30	0.60	0.29
7/25/2012	Carter 3	high	5617	8.03	290	0.18	0.29	0.14	33.82	2.07	1.60
8/20/2012	Carter 3	high	5646	7.92	320	0.15	0.28	0.20	45.29	2.19	1.76
12/10/2012	Carter 3	high	5733	7.76	270	0.38	0.21	0.44	38.73	1.10	0.51
4/21/2013	Carter 3	high	5837	8.78	390	0.17	0.19	0.21	51.04	1.21	0.85
5/22/2013	Carter 3	high	5907	8.13	110	0.25	0.25	0.25	11.62	1.63	1.13
10/21/2012	Carter 4	low	5688	7.77	1200	0.11	0.23	0.05	74.44	1.09	0.75
2/22/2013	Carter 4	low	5772	8.45	610	0.11	0.22	0.02	39.46	0.73	0.40
3/29/2013	Carter 4	low	5850	9.09	675	2.24	0.31	0.03	54.04	2.64	0.09
6/17/2013	Carter 4	low	5934	7.85	1080	0.20	0.31	0.52	29.51	2.22	1.70
7/13/2012	Carter 4	high	5608	7.68	770	0.11	0.21	0.05	10.06	0.70	0.37
9/17/2012	Carter 4	high	5653	7.74	490	0.20	0.21	0.16	61.77	1.18	0.78
12/10/2012	Carter 4	high	5734	7.52	840	0.19	0.21	0.06	32.44	0.81	0.40

4/21/2013	Carter 4	high	5838	9.03	530	1.27	0.28	0.10	58.90	2.62	1.07
5/22/2013	Carter 4	high	5908	8.10	120	0.23	0.23	0.19	14.30	1.73	1.27
10/21/2012	Carter 5	low	5689	8.17	1240	23.62	0.23	3.48	40.08	24.79	0.94
11/25/2012	Carter 5	low	5724	8.21	1240	24.20	0.21	4.06	39.07	25.13	0.71
1/27/2013	Carter 5	low	5761	8.18	1510	24.39	0.26	3.54	103.93	38.60	13.95
2/22/2013	Carter 5	low	5773	8.43	1380	20.70	0.21	3.30	69.30	21.53	0.62
3/29/2013	Carter 5	low	5851	8.09	1275	25.50	0.26	3.82	80.26	25.52	-0.24
6/17/2013	Carter 5	low	5935	8.23	1230	18.65	0.22	3.40	9.33	20.17	1.30
7/13/2012	Carter 5	high	5609	7.89	870	9.45	0.24	1.48	60.78	9.77	0.08
7/25/2012	Carter 5	high	5618	8.65	1160	17.06	0.21	3.42	41.96	16.40	-0.86
8/20/2012	Carter 5	high	5648	8.08	1045	12.99	0.27	2.38	82.90	20.57	7.30
9/17/2012	Carter 5	high	5654	7.92	280	0.27	0.20	0.17	47.67	1.60	1.13
12/10/2012	Carter 5	high	5735	7.85	625	3.03	0.56	0.95	40.60	3.72	0.14
4/21/2013	Carter 5	high	5839	8.3	1220	24.46	0.24	3.81	73.40	28.27	3.58
5/22/2013	Carter 5	high	5909	7.92	130	0.26	0.26	0.36	13.58	2.11	1.59
7/13/2012	Country Club	high	5603	7.81	510	0.13	0.33	0.19	53.24	1.45	0.99
9/17/2012	Country Club	high	5661	7.76	690	0.10	7.58	1.22	93.15	12.44	4.75
2/22/2013	Country Club	low	5780	8.1	760	0.08	0.21	0.16	59.49	1.12	0.83
6/17/2013	Country Club	low	5942	7.92	410	0.19	0.18	0.28	14.89	0.92	0.55
12/10/2012	Country Club	high	5742	7.72	340	0.37	0.22	0.47	45.35	1.43	0.84
4/21/2013	Country Club	high	5846	8.14	500	0.17	0.22	0.06	62.04	1.19	0.81
5/22/2013	Country Club	high	5916	7.68	240	0.20	0.17	0.19	16.22	1.60	1.24

APPENDIX B

STAGNANT STREAM SAMPLES COLLECTED BETWEEN JULY 2012 AND JUNE 2013 REMOVED FROM ANALYSIS

Month	Sample name
7/25/2012	Burton 2
7/25/2012	Burton 4
7/25/2012	Carter 1
7/25/2012	Carter 2
7/25/2012	Briar 2
8/20/2012	Carter 1
8/20/2012	Carter 4
8/20/2012	Country Club
9/17/2012	Carter 3
10/21/2012	Burton 2
10/21/2012	Carter 2
10/21/2012	Carter 3
10/21/2012	Country Club
11/25/2012	Carter 3
11/25/2012	Briar 2
11/25/2012	Carter 2
11/25/2012	Carter 3
11/25/2012	Carter 4
11/25/2012	Burton 2
11/25/2012	Country Club
4/21/2013	Carter 1
6/17/2013	Burton 1

APPENDIX C

RESULTS OF CLUSTER ANALYSIS (18 CLUSTERS) USING EUCLIDEAN DISTANCE FOR DR-NIR SOURCE SPECTRA OF STREAMS AND WATERSHED SOURCES

Source	Sample	ID #	% in Cluster	Cluster Analysis Number									
				1	2	3	4	5	6	7	8	9	10
Urban Soil	w5906	192	100	0	19	12	3	9	19	12	14	3	3
	w5907	193	100	0	19	12	3	9	19	12	14	3	3
	w5908	194	100	0	19	12	3	9	19	12	14	3	3
	w5909	195	100	0	19	12	3	9	19	12	14	3	3
	w5910	196	100	0	19	12	3	9	19	12	14	3	3
	w5911	197	100	0	19	12	3	9	19	12	14	3	3
	w5912	198	100	0	19	12	3	9	19	12	14	3	3
	w5913	199	100	0	19	12	3	9	19	12	14	3	3
	w5914	200	100	0	19	12	3	9	19	12	14	3	3
	w5915	201	100	0	19	12	3	9	19	12	14	3	3
	w5916	202	100	0	19	12	3	9	19	12	14	3	3
	w5649	112	60	1	9	11	5	2	12	0	19	13	18
	w5639	104	80	1	15	2	5	2	12	0	19	13	18
	w5645	109	70	1	15	2	5	12	12	0	19	13	18
	w5640	105	60	1	15	10	5	12	12	0	19	13	18
	w5641	106	60	1	15	10	5	12	12	0	19	13	18
	w5642	107	70	1	15	10	5	12	12	9	19	13	18
	w5648	111	70	1	15	11	5	2	12	0	19	13	18
	w5646	110	60	1	15	11	5	12	12	0	19	13	18
	Commercial Strip	61	90	1	15	2	5	2	12	0	19	13	8
	Commercial Strip	43	90	1	15	2	5	2	12	0	19	13	8
	Commercial Strip	44	100	1	15	2	5	2	12	9	19	13	8
	Commercial Strip	47	100	1	15	2	5	2	12	9	19	13	8
	Residential Lawn	48	100	1	15	2	5	2	12	9	19	13	8
	City Park	51	100	1	15	2	5	2	12	9	19	13	8
	Golf Course	54	100	1	15	2	5	2	12	9	19	13	8
	w5731	137	70	16	15	10	5	2	12	9	19	13	18
	w5724	131	60	16	15	10	5	12	12	9	19	13	18
	w5729	136	60	16	15	10	5	12	12	9	19	13	18
	w5733	139	60	16	15	10	5	12	12	9	19	13	18

	w5734	140	60	16	15	10	5	12	12	9	19	13	18
	w5735	141	60	16	15	10	5	12	12	9	19	13	18
	w5736	142	60	16	15	10	5	12	12	9	19	13	18
	w5737	143	60	16	15	10	5	12	12	9	19	13	18
	w5739	145	60	16	15	10	5	12	12	9	19	13	18
	w5740	146	60	16	15	10	5	12	12	9	19	13	18
	w5741	147	60	16	15	10	5	12	12	9	19	13	18
	w5742	148	60	16	15	10	5	12	12	9	19	13	18
	w5722	130	50	16	15	10	18	12	12	9	19	13	18
	w5725	132	50	16	15	10	18	12	12	9	19	13	18
	w5726	133	50	16	15	10	18	12	12	9	19	13	18
	w5727	134	50	16	15	10	18	12	12	9	19	13	18
	w5738	144	50	16	15	10	18	12	12	9	19	13	18
	w5598	87	60	16	15	11	5	2	12	0	19	13	18
	w5732	138	60	16	15	11	5	12	12	9	19	13	18
Effluent	EF1	10	70	2	7	9	10	16	3	6	7	14	13
	EF4	14	70	2	7	9	10	16	3	6	7	14	13
	EF2	12	100	2	7	15	11	10	3	6	7	14	13
	EF3	13	100	2	7	15	11	10	3	6	7	14	13
Runoff	RO1	15	100	2	7	15	11	10	3	8	7	14	13
	RO2	16	100	2	7	15	11	10	3	8	7	14	13
	RO3	17	100	2	7	15	11	10	3	8	7	14	13
	RO9	19	100	2	7	15	11	10	3	8	7	14	13
CM Feces	Cliff Martin	9	100	2	17	15	11	18	3	8	7	14	12
	Cliff Martin	11	100	2	17	15	11	18	3	8	7	14	12
	Impervious RO	18	100	2	17	15	11	18	3	8	7	14	12
	w5840	184	80	19	17	15	11	18	18	8	7	14	12
Tap	TAP	6	100	2	19	3	12	19	3	6	14	12	13
	TAP	7	100	2	19	3	12	19	3	6	14	12	13
	TAP	8	100	2	19	3	12	19	3	6	14	12	13
Human	Mammal Decomposition	38	100	3	13	18	15	6	14	1	12	9	16
Urban Soil	w5599	88	70	4	9	2	5	2	7	0	8	2	8
	w5762	151	70	4	9	19	4	2	7	5	8	16	5
	w5767	156	70	4	9	19	4	2	7	5	8	16	5
	w5757	149	70	4	9	19	5	2	7	5	8	16	5
	w5608	97	80	4	9	4	10	2	7	5	8	2	5
	w5602	91	80	4	9	19	5	2	7	5	8	16	5
	w5764	153	80	4	9	19	5	2	7	5	8	16	5
	w5765	154	80	4	9	19	5	2	7	5	8	16	5

	w5603	92	90	4	9	11	4	2	7	5	8	2	5
	w5776	164	90	4	9	11	5	2	7	0	8	2	5
	w5777	165	90	4	9	11	5	2	7	0	8	2	5
	w5778	166	90	4	9	11	5	2	7	0	8	2	5
	w5779	167	90	4	9	11	5	2	7	0	8	2	5
	w5605	94	100	4	9	11	5	2	7	5	8	2	5
	w5609	98	100	4	9	11	5	2	7	5	8	2	5
	Commercial Strip	46	100	4	9	11	5	2	7	5	8	2	5
Effluent	EF5	20	100	5	5	13	0	0	5	19	15	5	10
	EF6	21	100	5	5	13	0	0	5	19	15	5	10
	EF7	22	100	5	5	13	0	0	5	19	15	5	10
	EF8	23	100	5	5	13	0	0	5	19	15	5	10
	EF9	24	100	5	5	13	0	0	5	19	15	5	10
	EF10	25	100	5	5	13	0	0	5	19	15	5	10
	EF11	26	100	5	5	13	0	0	5	19	15	5	10
	EF12	27	100	5	5	13	0	0	5	19	15	5	10
	EF13	28	100	5	5	13	0	0	5	19	15	5	10
	EF14	29	100	5	5	13	0	0	5	19	15	5	10
Urban Soil	Golf Course	41	100	6	1	5	8	5	17	3	11	15	2
	City Park	57	100	6	1	5	8	5	17	3	11	15	2
	City Park	82	90	6	1	5	8	7	17	3	11	15	2
	City Park	52	70	6	2	5	8	7	17	3	1	19	2
	Residential Lawn	78	70	6	2	5	8	7	17	3	1	19	2
	City Park	81	60	6	2	5	8	7	17	3	1	19	2
	Retention Pond	79	60	6	0	14	6	17	0	3	11	15	2
Grass Park	w5853	175	40	8	8	11	4	14	9	7	9	6	15
	w5643	108	90	8	9	11	4	2	7	5	9	1	5
	w5851	173	70	8	9	11	4	14	7	7	9	2	5
	w5854	176	70	8	9	11	4	14	7	7	9	2	5
	w5847	169	50	8	9	11	4	14	9	7	9	2	18
	w5850	172	50	8	9	11	4	14	9	7	9	2	18
	w5852	174	50	8	9	11	4	14	9	7	9	2	18
	w5870	178	50	8	9	11	4	14	9	7	9	2	18
	w5848	170	50	8	9	11	4	14	9	7	9	13	18
	w5871	179	50	8	9	11	4	14	9	7	9	13	18
	w5849	171	70	8	9	11	4	14	9	7	9	16	5
	w5855	177	50	8	9	11	4	14	9	7	9	17	18
	w5604	93	60	8	9	11	5	2	12	5	6	13	18
	w5600	89	60	8	9	11	5	2	12	5	9	13	18

	w5761	150	80	8	9	19	5	2	7	5	9	16	5
	w5763	152	80	8	9	19	5	2	7	5	9	16	5
	w5766	155	80	8	9	19	5	2	7	5	9	16	5
	City Park	80	100	8	9	11	4	2	7	5	9	16	5
Runoff	w5933	205	30	8	14	0	14	11	15	11	9	18	8
	w5931	203	30	8	14	1	19	5	16	11	9	17	7
	Impervious RO	83	100	8	8	11	18	17	6	11	9	6	18
Impervious Runoff	w5651	113	100	11	0	14	6	17	0	13	10	6	15
	w5659	120	100	11	0	14	6	17	0	13	10	6	15
	w5661	122	100	11	0	14	6	17	0	13	10	6	15
	w5685	126	100	11	0	14	6	17	0	13	10	6	15
	w5728	135	100	11	0	14	6	17	0	13	10	6	15
	w5682	123	60	11	8	10	18	17	9	13	10	6	15
	w5652	114	90	11	8	14	6	17	0	13	10	6	15
	w5653	115	90	11	8	14	6	17	0	13	10	6	15
	w5654	116	90	11	8	14	6	17	0	13	10	6	15
	w5656	118	90	11	8	14	6	17	0	13	10	6	15
	w5660	121	90	11	8	14	6	17	0	13	10	6	15
	w5683	124	90	11	8	14	6	17	0	13	10	6	15
	w5688	127	90	11	8	14	6	17	0	13	10	6	15
	w5655	117	70	11	8	14	18	17	6	13	10	6	15
	w5658	119	70	11	8	14	18	17	6	13	10	6	15
	w5690	129	70	11	8	14	18	17	9	13	10	6	15
	Grass Comm Strip	75	60	11	0	14	1	5	0	10	10	17	15
	Grass Golf Course	73	70	11	0	14	1	5	0	13	10	17	15
	Impervious RO	85	100	11	0	14	6	17	0	13	10	6	15
	Impervious RO	86	100	11	0	14	6	17	0	13	10	6	15
	Grass City Park	77	80	11	0	14	6	17	0	13	11	15	15
	Impervious RO	84	70	11	8	14	18	17	6	13	10	6	15
Urban Soil	w5618	103	90	12	6	1	19	5	16	10	5	7	7
	w5612	100	100	12	6	1	19	5	16	10	6	7	7
	w5614	101	100	12	6	1	19	5	16	10	6	7	7
	w5601	90	80	12	6	1	19	5	16	10	6	17	18
	w5606	95	80	12	6	1	19	5	16	10	6	17	18
	w5607	96	80	12	6	1	19	5	16	10	6	17	18
	w5610	99	90	12	6	1	19	5	16	10	11	7	7
	Grass Comm Strip	76	60	12	0	1	1	5	16	10	11	17	7
	City Park	59	70	12	6	1	1	5	16	10	5	17	7

	City Park	50	70	12	6	1	1	5	16	10	6	17	7
	City Park	56	70	12	6	1	1	5	16	10	6	17	7
	City Park	58	70	12	6	1	1	5	16	10	11	17	7
	City Park	45	80	12	6	1	19	5	4	10	5	7	7
	City Park	55	80	12	6	1	19	5	4	10	5	7	7
	Wetland	42	90	12	6	1	19	5	16	10	5	7	7
	Residential Lawn	40	100	12	6	1	19	5	16	10	6	7	7
	City Park	53	100	12	6	1	19	5	16	10	6	7	7
	Residential Lawn	39	80	12	6	1	19	5	16	10	11	15	7
Feces	Racing Pigeon	1	100	13	16	7	17	8	13	4	3	8	9
	Cow	2	100	13	16	7	17	8	13	4	3	8	9
	Chicken 1	3	100	13	16	7	17	8	13	4	3	8	9
	Chicken 2	4	100	13	16	7	17	8	13	4	3	8	9
	Dog	5	100	13	16	7	17	8	13	4	3	8	9
	Soil Commercial	72	90	13	16	7	17	8	17	4	3	8	9
Runoff	RO11	32	40	14	5	13	0	0	5	19	15	5	10
	RO7	33	70	14	5	13	0	1	1	19	15	5	17
	RO4	34	100	14	5	13	16	1	1	19	4	4	17
	RO5	35	100	14	5	13	16	1	1	19	4	4	17
	RO6	36	100	14	5	13	16	1	1	19	4	4	17
	RO10	37	100	14	5	13	16	1	1	19	4	4	17
Retention Pond	w5617	102	90	15	1	1	10	16	4	10	5	7	7
	w5769	157	30	15	3	4	10	13	2	6	18	12	19
	w5770	158	30	15	3	4	10	13	2	6	18	12	19
	w5771	159	30	15	3	4	10	13	2	6	18	12	19
	w5772	160	30	15	3	4	10	13	2	6	18	12	19
	w5773	161	30	15	3	4	10	13	2	6	18	12	19
	w5774	162	30	15	3	4	10	13	2	6	18	12	19
	w5780	168	30	15	3	4	10	13	2	6	18	12	19
	w5775	163	40	15	3	4	10	13	4	6	18	1	19
	Grass City Park	60	80	15	6	1	10	16	4	10	5	7	7
	Soil Ret Pond	49	100	15	1	4	10	16	4	10	5	7	7
	Veg Vetland	74	20	15	1	5	8	7	17	3	1	19	2
Native Soil	Urban Landscape	62	100	17	10	9	13	19	10	16	0	10	0
	Remnant Forest	63	100	17	10	9	13	19	10	16	0	10	0
	Remnant Forest	64	100	17	10	9	13	19	10	16	0	10	0
	Remnant Forest	65	100	17	10	9	13	19	10	16	0	10	0
	Wetland	66	100	17	10	9	13	19	10	16	0	10	0
	Wetland	67	100	17	10	9	13	19	10	16	0	10	0

	Wetland	68	100	17	10	9	13	19	10	16	0	10	0
	Shrub-Scrub	69	100	17	10	9	13	19	10	16	0	10	0
	Shrub-Scrub	70	100	17	10	9	13	19	10	16	0	10	0
	Shrub-Scrub	71	100	17	10	9	13	19	10	16	0	10	0
OIL	OIL	30	100	18	11	16	7	15	8	15	16	0	6
	OIL	31	100	18	11	16	7	15	8	15	16	0	6
No Cluster with known landscape spectra	w5684	125		16	8	10	18	12	9	13	10	6	15
	w5689	128		16	8	10	18	12	9	13	10	6	15
	w5932	204		9	18	8	9	3	11	14	17	11	11
	w5934	206		9	18	8	9	3	11	14	17	11	11
	w5936	208		9	18	8	9	3	11	17	17	11	11
	w5938	210		9	18	8	9	3	11	17	17	11	11
	w5940	212		9	18	17	9	3	11	17	17	11	11
	w5942	214		9	18	17	9	3	11	17	17	11	11
	w5836	180		10	12	6	2	4	18	18	2	3	1
	w5837	181		10	12	6	2	4	18	18	2	3	4
	w5838	182		10	12	6	2	4	18	18	2	3	4
	w5839	183		10	12	6	2	4	18	18	2	3	4
	w5842	186		10	12	6	2	4	18	18	2	3	4
	w5843	187		10	12	6	2	4	18	18	2	3	4
	w5844	188		10	12	6	2	4	18	18	2	3	4
	w5845	189		10	12	6	2	4	18	18	2	3	4
	w5846	190		10	12	6	2	4	18	18	2	3	4
	w5905	191		10	19	3	3	9	19	12	14	3	3
	w5841	185		19	12	6	2	4	18	18	2	3	4
	w5935	207		7	4	0	14	11	15	2	13	18	14
	w5937	209		7	4	0	14	11	15	2	13	18	14
	w5939	211		7	4	0	14	11	15	2	13	18	14
	w5941	213		7	14	0	14	11	15	2	13	18	14