SOURCES AND FATES OF DISSOLVED ORGANIC CARBON IN RURAL AND URBAN WATERSHEDS IN BRAZOS COUNTY, TEXAS

A Thesis

by

DANIELLE MARIE CIOCE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2012

Major Subject: Water Management and Hydrologic Science

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in Rural and Urban Watersheds in Brazos County, Texas

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Approved by:

Chair of Committee,	Jacqueline Aitkenhead-Peterson
Committee Members,	Thomas Boutton
	Bradford Wilcox
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ABSTRACT

Sources and Fates of Dissolved Organic Carbon
in Rural and Urban Watersheds in Brazos County, Texas. (August 2012)
Danielle Marie Cioce, B.S., Dickinson College
Chair of Advisory Committee: Dr. Jacqueline Aitkenhead-Peterson

The Bryan/College Station (B/CS) region has been reported to have elevated concentrations of dissolved organic carbon (DOC) in surface water. Increased DOC concentrations are worrisome as DOC has been shown to be an energy source for the recovery and regrowth of *E. coli* and many watersheds are impaired by high bacteria levels. To examine the sources and fates of DOC in rural and urban regions to better understand DOC movement though the environment, seven watersheds were studied. To investigate source, streams were analyzed using diffuse reflectance near infrared spectroscopy (DR-NIR) and carbon isotopes. Fate of DOC was determined through monthly streams samples, gathered between March 2011 and February 2012, which were incubated for biodegradable DOC (BDOC). Soil in the region was sampled based on land use categories. Soil was analyzed for DOC and BDOC as well as DOC adsorption, the other major fate of DOC. Above ground vegetation was sampled in conjunction with soil and analyzed for BDOC.

Data indicated that fecal matter from cliff swallows provided considerable organic material to streams in the B/CS region as shown through DR-NIR. Carbon isotope values in streams ranged from -23.5±0.7‰ to -26.8±0.5‰. Stream spectra may be able to predict carbon isotope values in streams (Adj. $R^2 = 0.88$). Mean annual stream DOC concentrations ranged from11±3 mg/L to 31±12 mg/L, which represents a significant decrease in DOC between 2007 and 2011. Concurrent increases in pH and conductivity were also recorded. The decrease in DOC and the increases in pH and conductivity may be due to impacts of high sodium irrigation tap water. Biodegradable DOC was low in streams, which is likely due to DOC being present in streams in refractory forms that are resistant to microbial breakdown. Soil chemistry, including soil adsorption, was greatly influenced by sodium. The elevated adsorption coefficients and release values seen in highly developed and urban open areas can be attributed to frequent exposure to high sodium irrigation water. The results indicate that sodium is a major driver of DOC in the system. Sound management decisions concerning irrigation water chemistry and urban development might eventually emerge to protect water quality as a result of this research.

DEDICATION

This thesis is dedicated to the memory of Dr. Valeen “Val” Silvy, a dearly missed mentor and friend.

“You can’t stop the waves, but you can learn to surf.”

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I would like to thank my advisor and committee chair, Dr. Jacqueline Aitkenhead-Peterson, for her encouragement and guidance. Dr. Thomas Boutton and Dr. Bradford Wilcox served on my committee and supported this research through valuable feedback and comments. Thanks goes to Stephen Sweet of the Geochemical and Environmental Research Group (GERG) at Texas A&M University, who graciously freeze dried samples in preparation for isotope analysis. The Stable Isotope Biosphere Science laboratory (SIBS), under the direction of Dr. Thomas Boutton, analyzed isotope samples. Thanks also to Greg Wall and other staff members of Carters Creek Waste Water Treatment Plant of the City of College Station who allowed monthly effluent sampling at their facility. Many thanks go to my colleagues at the Nutrient and Water Analysis (NAWA) research laboratory, and especially to Nina Stanley for her assistance in laboratory and field work.

I am appreciative for the funding that allowed this research to take place, which included a Diversity Fellowship from the Office of Graduate Studies at Texas A&M University, a Mills Scholarship from the Texas Water Resources Institute, and support from the Water Management and Hydrologic Sciences program at Texas A&M University.

NOMENCLATURE

B/CS	Bryan/College Station
BDOC	Biodegradable dissolved organic carbon
DDW	Distilled deionized water
DOC	Dissolved organic carbon
DOC_{eq}	Equilibrium dissolved organic carbon
DOM	Dissolved organic matter
DR-NIR	Diffuse reflectance near infrared spectroscopy
EC	Electrical conductivity
HSG	Hydrologic soil group
$NaHCO_3$	Sodium bicarbonate
NLCD	National Land Cover Database
NRCS	Natural Resources Conservation Service
RCN/CN	Runoff curve number/curve number
RSP	Reactive soil pool
SAR	Sodium adsorption ratio
SCS	Soil Conservation Service
TCEQ	Texas Commission on Environmental Quality
USGS	United States Geological Survey
WEDOC	Water extractable dissolved organic carbon
WWTP	Waste water treatment plant

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INTRODUCTION

Dissolved organic matter

Dissolved organic matter (DOM) is made up of many complex organic molecules containing carbon (dissolved organic carbon: DOC), nitrogen (dissolved organic nitrogen: DON), phosphorus (dissolved organic phosphorus: DOP), and sulfur (dissolved organic sulfur: DOS) (Aitkenhead-Peterson et al. 2003). Dissolved organic carbon is the largest subset in the DOM pool (Benner 2003). Dissolved organic matter is defined as the portion of organic matter that will pass through a filter with pore size of less than 0.45 µm (Thurman 1985). In practice, it is considered to be organic material that will pass through a 0.7 µm filter by many laboratories due to complications with carbon contamination from 0.45 µm cellulose filters. Dissolved organic matter typically consists of organic material produced from dissolved atmospheric gases and dusts in precipitation, organic matter from vegetation leached as throughfall, root exudates, root and leaf litter, and both the primary and secondary metabolites of microorganisms (Aitkenhead-Peterson et al. 2003).

Zsolnay (2003) stated that the scientific community is realizing that DOM is involved in numerous ecological processes, such as climate change, desertification, pollution impact, and water quality. Dissolved organic matter is crucial in aquatic systems as it provides an energy source for biota and protects aquatic life from UV light (Williamson and Zagarese 1994; Leenheer and Croue 2003). It is also responsible for the complexation, solubility, and mobility of metals and pesticides in surface waters (Martell et al. 1988; Worrall et al. 1997). The concentration of DOM in surface waters varies according to the source of organic matter (autochthonous vs. allochthonous), temperature, ionic strength, pH, cation composition, surface chemistry of sediment, and photolytic and microbial degradation processes (Leenheer and Croue 2003). It is thought that most DOM in streams is derived from allochthonous sources (Sanderman et

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This thesis follows the style of Biogeochemistry.

al. 2009). Terrestrial, or allochthonous, DOM is typically supplied to streams by soils and leaf litter (Aitkenhead-Peterson et al. 2003). Thus, the advance of both global land use and climate change may continue to influence and increase concentrations of organic matter in surface waters (Findlay and Sinsabaugh 1999; Evans et al. 2005). Soil is an important regulator for DOM in streams as the concentration of DOM in surface waters is dependent on the flow path through soil, biodegradation in soil (Marschner and Kalbitz 2003; McDowell et al. 2006), and the capacity of the mineral soil to adsorp DOM (Aitkenhead-Peterson et al. 2003).

Biodegradability of dissolved organic carbon

Biodegradability of DOM is defined "as the utilization of compounds by microorganisms as measured through the disappearance of DOM or O_2, or by the evolution of CO_2" (Marschner and Kalbitz 2003). Dissolved organic matter biodegradability is controlled by many factors in three categories: intrinsic quality, soil properties, and external factors (Marschner and Kalbitz 2003). Intrinsic DOM qualities consist of molecular structure and size, as well as functional group content. Soil characteristics, such as the microbial community structure and nutrient availability, can have an effect on biodegradation (Marschner and Kalbitz 2003), but not always (McDowell et al. 2006). In a study examining biodegradability in throughfall and various soils, McDowell et al. (2006) reported that the source and community structure of microbes used in batch experiments to degrade DOM did not matter, but nutrient availability was important to the extent of degradation. Lastly, external factors such as temperature, precipitation, and vegetation can create seasonal variations of microbial activity and inputs of DOM, thus influencing biodegradability (Marschner and Kalbitz 2003).

Dissolved organic carbon (DOC), the largest subset of the DOM pool, is largely composed of humic substances, most of which are fulvic acids (Aitkenhead-Peterson et al. 2003; Benner 2003). The terms DOC and DOM are often used interchangeably, likely due to the minor contribution of DON, DOP, and DOS to the total DOM pool. Hydrophilic acids and low molecular weight organics, such as simple carbohydrates (for example, glucose or fructose), and carboxylic and amino acids are also present (Aitkenhead-Peterson et al. 2003). Dissolved organic matter typically consists of both a labile, rapidly degradable fraction and a refractory, slowly degradable fraction which has been shown to remain in solution for up to 180 days (Marschner and Kalbitz 2003). The labile portion of DOM is composed of simple carbohydrates, low-molecular organic acids (such as citric or oxalic acid) and proteins, amino acids, and sugars (Marschner and Kalbitz 2003). The refractory portion of DOM is thought to contain polysaccharides or other compounds derived from plants or microbes that need certain enzymes for degradation (Marschner and Kalbitz 2003). Labile DOC is often consumed by microbes in the soil, while refractory DOC is usually sorbed to mineral soil below the organic layer (Aitkenhead-Peterson et al. 2003). Biodegradability of DOM is increased in soils or solutions with high concentrations of carbohydrates, organic acids, and proteins, and decreased by aromatic and hydrophobic structures (Marschner and Kalbitz 2003). Studies have indicated that biodegradable DOC (BDOC) in surface water can vary from 4-68% (Wiegner and Seitzinger 2001; Seitzinger et al. 2005; Wiegner et al. 2006).

Little research has been conducted on the bioavailability of DOC in urban freshwater systems (Harbott and Grace 2005). It has been shown that urbanization can increase both dissolved and particulate organic carbon, but decrease the retention of organic matter in streams (Paul and Meyer 2001). Urban streams with waste water treatment plants tend to have less variable and higher concentrations of DOC (Westerhoff and Anning 2000), but this depends on the relative release of DOC from the watershed in relation to DOC released as point source effluent (Aitkenhead-Peterson et al. 2009).

A study examining a beech forest floor found mean BDOC of 39% for a 21 day incubation of soil water extract (Andreasson et al. 2009). Soil solution was found to be 16-68% biodegradable during a three month incubation at room temperature (Zsolnay and Steindl 1991). Another study found soil solution BDOC to be 27% during a 134 day incubation (Qualls and Haines 1992). A bioreactor method with an incubation time of five hours reported that BDOC of soil solution collected by zero tension lysimeters under the forest floor of coniferous and hardwood stands ranged from 17-45% (Yano et al. 1998). However, BDOC studies tend to have a wide variety of methodologies for incubation. A group of researchers in the United States and Europe shared six different soil extracts, soil solutions, and throughfall solutions to quantify BDOC using different methods (McDowell et al. 2006). Overall, large differences among the methods used to determine BDOC were not found (McDowell et al. 2006).

Bioavailable DOC has also been shown to decrease with soil depth (Boyer and Groffman 1996). Greater bioavailable DOC was found in cornfields than in forest soils (Boyer and Groffman 1996). Results from a study on freshwater wetlands suggested that seasonality and anthropogenic activity altered the bioavailability of DON in runoff, but seasonal patterns for DOC were not as clear (Wiegner and Seitzinger 2004).

Soil chemistry

Soil is important in understanding DOC as it is a source of transformed organic material. Changes in land use and land cover can affect DOM cycling by shifting inputs of organic matter, altering soil substrate quality, and adjusting microbial degradation through changes in pathway, rate, and range (Cronan et al. 1992). Watersheds with a high distribution of wetlands have been shown to have increased DOC concentrations in streams (Dillon and Morlot 1997; Aitkenhead et al. 1999; Williams et al. 2005; Mattson et al. 2005; Aitkenhead-Peterson et al. 2007). Turfgrass lawns often found in residential and commercial areas may be exposed to increased inputs of organic matter or fertilizer which will increase the carbon available to the system (Steele and Aitkenhead-Peterson 2012b). Soil carbon is more likely to be sequestered under urban turfgrass compared to agricultural soils with conventional tillage (Morgan et al. 2010).

Organic matter in soil is derived from the breakdown and transformation of leaf litter, root decay and exudates, and death and decay products of animals and microbes (Aitkenhead-Peterson et al. 2003). Microbes are important in the processing of organic matter in soil and are typically regarded as the controlling factor for litter decomposition, leaching of organic matter from litter, and the creation of humic substances (Kalbitz et al. 2000). Abiotic processes, such as adsorption and precipitation, may largely control the concentration of DOM in soil solution (Kalbitz et al. 2000). Changes in DOM in soil solution are thought to be tied to the amount of litter recently deposited on the surface and the total indigenous organic matter present in the soil (Kalbitz et al. 2000). Accordingly, the quality of litter is determined by the vegetation at the site and the importance of vegetation as a controlling factor for DOM concentrations in soil should not be overlooked (Kuiters 1993).

It has been previously reported that an increase in soil pH of 0.5 units would cause a 50% increase in DOM mobilization (Tipping and Woof 1990). Numerous laboratory studies have documented an increase in DOC release from soil with raised pH (Whitehead et al. 1981; Hay et al. 1985; Tipping and Hurley 1988; Gödde et al. 1996; Jozefaciuk et al. 1996; Kennedy et al. 1996; Hajnos et al. 1999; You et al. 1999). However, the interactions of pH and DOM in the field appear to be minor (Kalbitz et al. 2000).

Biogeochemical cycling of organic material in soil is thought to have a spatial and seasonal effect on the concentration and composition of DOC in surface water (Sanderman et al. 2009). Organic matter in soil varies “somewhat predictably”, thus DOM can potentially be used as a “tracer of source water and runoff generation pathways” based on its chemical composition (Sanderman et al. 2009). Typically DOC concentrations in soil solutions from the A horizon were reported to be between 5 and 50 mg/L and decrease with depth (Herbert and Bertsch 1995). Another study in New Hampshire forest soils found an average of 33 mg/L DOC in the A2 horizon compared to 2-3 mg/L in the B horizon (McDowell and Wood 1984). Soil DOC has been shown to increase in response to rewetting after a dry cycle (McDowell and Wood 1984; Zabowski and Ugolini 1990; Haynes and Swift 1991; Chittleborough et al. 1992; Kalbitz and Knappe 1997; Lundquist et al. 1999; Tipping et al. 1999; Zsolnay et al. 1999). Three possible reasons for this were proposed by Lundquist et al. (1999): a reduction in the use of DOC by microbes during dry periods, an increased overturn of microbial biomass via rewetting, or a change in soil structure that could allow for carbon sequestered previously to become bioavailable. Not all soils respond similarly to wet and dry cycles. Microbes in soils under oak trees were found to undergo changes in community composition, while soil microbes under grass did not have a shift in population (Fierer et al. 2003). The differences in microbial community response were attributed to greater exposure to moisture stress in grass environments, and therefore greater adaptation to change (Fierer et al. 2003). Soil anaerobic conditions due to saturation with water have also been shown to increase DOM release (Mulholland et al. 1990; Sedell and Dahm 1990).

Soil adsorption

Soil adsorption is often regarded as more important than decomposition in reducing concentrations of DOC in soil solution (Kalbitz et al. 2000). Soil can retain a "considerable portion" of solution DOC through adsorption to soil mineral surfaces (McDowell and Wood 1984; Dalva and Moore 1991; Moore et al. 1992; Kalbitz et al. 2003). Organic carbon concentrations, iron and aluminum content, and soil mineralogy influence the extent of DOC adsorption (Moore et al. 1992). Clay soils have been shown to be positively related to adsorption of DOC as well as to runoff in watersheds with high clay content soils, which have lower DOC concentrations (Nelson et al. 1993; Kalbitz et al. 2000). The presence of aluminum and iron oxides and hydroxides in soils also increases DOC adsorption (Moore et al. 1992; Kalbitz et al. 2000). For example, it was found that 72 to 92% of DOC adsorped to iron oxides was "irreversibly bound" (Gu et al. 1994). It is important to note however that there is a maximum for DOC adsorption in soil, which depends on both the indigenous carbon in the soil as well as the surface area of the dominant soil minerals (Moore et al. 1992; Vance and David 1992; McCracken et al. 2002). After the adsorption maximum is reached, carbon would be leached from soil due to a lack of available adsorption sites. Adsorption of DOC will be greater in soils with low indigenous adsorped carbon (Kalbitz et al. 2000). Low exports of carbon from clay soils high in aluminum and iron with low indigenous adsorped carbon would be expected (Kalbitz et al. 2000). Increased pH has been shown to decrease the capacity for soil adsorption (Kalbitz et al. 2000). An elevated pH will increase DOC release due to reduced carbon mineralization. Solubility of DOC will also be increased with elevated pH due to protonation of DOC functional groups (Kalbitz et al. 2000).

Mineral soil adsorption of DOM is typically quantified using the initial mass isotherm method of Nodvin et al. (1986). Results from studies examining adsorption in B horizon soils under forests in New Hampshire (Nodvin et al. 1986), a variety of Canadian soils from the A,B, and C horizons assumed to be forests using DOC derived from swamp peat (Moore et al. 1992), and agricultural soil to a depth of 15cm from Italy using DOC from farmyard manure (Riffaldi et al. 1998) are described in Table 1 for the adsorption coefficient (m), release term (b), and reactive soil pool (RSP). The adsorption coefficient was found to be positively correlated to soil clay content in agricultural soils ($r = 0.89$, $p = 0.001$) while the release term was positively correlated to soil DOC ($r = 0.87$, $p = 0.001$) (Riffaldi et al. 1998). Equilibrium DOC (DOC_{eq}), also known as null point DOC, is defined as the value at which there is no removal or release of DOC from solution and is typically regarded to be the intercept of the adsorption isotherm and y axis (Moore et al. 1992). Another study on Canadian soils found that soils with high clay content may have higher DOC_{eq} than sandy soils (Moore and Matos 1999). Moore et al. (1992) also reported that organic carbon, extractable aluminum, and extractable iron explained 70% of the variation seen in DOC_{eq}.

Table 1. Mean terms for adsorption coefficient (m), release term (b), and reactive soil pool (RSP) for adsorption studies. Data are based on the initial mass isotherm method of Nodvin et al. 1986. Ranges are given in parentheses.

	Nodvin et al. 1986	Moore et al. 1992	Riffaldi et al. 1998
m (unitless)	0.60	0.45 (0.15-0.78)	0.32 (0.09-0.60)
b (mg/kg)	29.8	142 (30-520)	127 (14-227)
RSP (mg/kg)	74.8	330 (50-1790)	199 (65-377)

Diffuse reflectance near infrared spectroscopy

Near infrared spectroscopy (NIR) is an optical analytical technique that has been widely used in agriculture, paper, food, manufacturing, and pharmaceutical industries for analysis of composition and function (Foley et al. 1998; Perrson et al. 2007). Near infrared spectroscopy describes the molecular composition of organic material in a sample as it 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) which allows for the molecular composition of organic material to be determined (Nilsson et al. 1996; Korsman et al. 2001). 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 are then usually combined in a predictive statistical model which may be used to predict the molecular composition of unknown samples (Foley et al. 1998). The accuracy of the model depends on the reference and calibration data, but NIR is "often more precise" than laboratory assays (Geladi and Dabakk 1995; Foley et al. 1998).

Near infrared spectroscopy has 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). The NIR method is preferable as it is a rapid, reagent free, and nondestructive quantitative method that requires limited sample preparation (Nilsson et al. 1996; Perrson et al. 2007). Additionally, the instrumentation is relatively affordable (Perrson et al. 2007). Using NIR allows for estimation of several parameters from one method, rather than a range of wet chemistry methods that require a lot of time, training, and reagents (Dabakk et al. 2000). This could allow for extensive long term environmental monitoring that is cost effective, accurate, and feasible given the limited staff of regulatory agencies (Dabakk et al. 2000; deMedeiros et al. 2005). Additionally, NIR could be used to detect events in near real time, allowing for regulatory agencies to respond quickly (deMedeiros et al. 2005).

The limited use of NIR in water research has focused on lake studies. For example, NIR was used to predict lake water chemistry (total organic carbon, total phosphorus, and pH, among other constituents) in Sweden based on scans 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 to reconstruct sediment and water chemistry (Korsman et al. 2001). It was found that NIR performed better than chemical and diatom analyses in a study examining epilithic material in streams impacted by mining in Sweden (Perrson et al. 2007).

An evaporative method has been developed that concentrates stream water samples and allows spectral signatures to be recorded (Steele and Aitkenhead-Peterson unpublished). Most studies utilize NIR spectroscopy as a predictive tool where a model is constructed with observed wet chemistry data and NIR spectra. A novel technique has been developed (Aitkenhead-Peterson unpublished) which utilizes the whole NIR spectra of stream water and examines its similarity to the NIR spectra of source organic materials within the watershed.

Carbon isotopes

Stable isotopes can be used to help determine the sources of organic matter to streams, as well as water flow path, nutrient cycling, and food web processes (Kendall and Doctor 2004; Finlay and Kendall 2007). Biological, chemical, and physical processes can cause fractionation, which forms differences in the proportion of isotopes in elements with low atomic numbers (Kendall and Doctor 2004). These isotopic differences become unique signatures that can be used to trace source material (Kendall and Doctor 2004). Isotopes are typically reported as delta (δ) values in parts per thousand (‰ or per mil) relative to a standard (Kendall and Doctor 2004).

Organic carbon tends to be depleted in ^{13}C, while inorganic carbon is enriched in ^{13}C (Boutton 1991). DOC tends to become enriched in ^{13}C during riverine transport due to additions from autochthonous inputs and removal from microbes and abiotic processes (Raymond and Bauer 2001). C_3 plants, which include deciduous and coniferous trees as well as cool season grasses such as ryegrass and fescue, have an approximate $\delta^{13}C$ value of -27‰, while C_4 plants, which include warm season grasses such as St. Augustine, have a $\delta^{13}C$ value of -13‰ (Boutton 1991; Finlay and Kendall 2007; Fountain 2012). Additionally, the ranges for C_3 and C_4 plants (-32 to -22‰ vs. -16 to-9‰, respectively) do not overlap, which allows for distinction between the two plant types to occur (Boutton 1991; Finlay and Kendall 2007). Soil organic matter typically has the signature of the vegetation above it (Boutton 1991; Kendall and Doctor 2004; Finlay and Kendall 2007). However, the $\delta^{13}C$ signature of soil organic matter may not correspond to its above ground vegetation if there has been recent change in vegetation and land use (Dzurec et al. 1985). In soils, $\delta^{13}C$ values decrease with depth, possibly due to the favored processing of compounds with higher $\delta^{13}C$ ratios (such as amino acids and carbohydrates) compared to compounds with lower $\delta^{13}C$ ratios (such as lignin and cellulose) (Schiff et al. 1990). Freshwater values for $\delta^{13}C$ have been reported to range from -18 to -46‰ (McKnight et al. 2003). A coastal watershed in California was found to have a range of $\delta^{13}C$ values from -24.2 to -28.9‰ (Sanderman et al. 2009). A watershed scale study in Ontario found $\delta^{13}C$ to vary from -27 to -40‰ in streams and wetlands (Schiff et al. 1990). It appears that streams do not reflect the C_4 plant signature based on the above studies. Research on DOC leaching from senesced vegetation showed that ryegrass, a C_3 plant, lost 2 to 4 times more DOC than St. Augustine grass, a C_4 plant, when exposed to high sodium water (Steele and Aitkenhead-Peterson 2012a). However, not all C_3 plants have increased DOC leaching, as live oak leaves (C_3) lost less DOC than St. Augustine grass (Steele and Aitkenhead-Peterson 2012a). Understanding the dynamics of the site specific vegetation may be important in interpreting carbon isotope values in streams.

Objectives

Three objectives were outlined for this study:

- Investigate the sources of stream water dissolved organic carbon using diffuse reflectance near infrared spectroscopy and carbon isotopes

- Determine the fates of dissolved organic carbon in rural and urban watersheds in Brazos County, Texas including a) the extent of biodegradation or immobilization by microbes, b) adsorption to soil and c) release to stream water
- Examine the extent of the relationships between land use, carbon isotopes of dissolved organic carbon, biodegradability of dissolved organic carbon, and soil adsorption

This research focused on developing a comprehensive understanding of the sources and fates of DOC. This was accomplished by analyzing a transition gradient of rural to urban watersheds in Brazos County, Texas. The first part of the study was to determine the source of DOC in each watershed, which was quantified by diffuse reflectance near-infrared spectroscopy and compared to results from stable carbon isotope analysis. The second part of the study was to examine the fate of DOC, including the extent of biodegradation or immobilization by microbes, the adsorption to soil minerals, and release to stream water. Biodegradability of DOC in soil under different land use was also quantified.

The third and final part of the study aimed to determine the extent of the relationships between land cover and use, biodegradability of DOC in streams and soil, adsorption of DOC to soil, and carbon isotopes of DOC. Seasonality was also investigated, as it would be expected that older, more refractory DOC is released from soil when subjected to intensive summer irrigation with municipal tap water. This would result in increased instream concentrations that would be significantly less biodegradable relative to DOC derived from streams downstream of waste water treatment plants or in rural watersheds.

This research aimed to explore the sources and fates of DOC to better understand the high concentrations reported in surface waters in the region. This is of vital importance because DOC has been shown to be an energy source for the recovery and regrowth of *E.coli* (Bolster et al. 2005; McCrary et al. in review) and many watersheds in Texas, as well as the nation, are currently impaired by high bacteria levels. Bacteria is the number one water quality concern in Texas, and 291 water bodies were listed as impaired for bacteria in the 2010 Texas Water Quality Integrated Report as described in the Clean Water Act's 303(d) list (TCEQ 2010).

Establishing the fate of DOC will lead to increased understanding of the impacts of transitioning land use and irrigation on water quality in Brazos County. The study incorporates both soil and surface water analysis, which allows for a more comprehensive and holistic view of carbon cycling within the region. Assessing the biodegradation of DOC in watersheds in Brazos County may be helpful in understanding the mechanisms contributing to elevated concentrations of organic matter and also to determine if land use has an effect on the source, biodegradability, and adsorption of DOC in soils and surface waters.

This research builds upon previous work which found that high sodium municipal tap water altered the community composition of microbes in soil and thus nutrient release (Holgate et al. 2011). Additionally, it was found that carbon from terrestrial sources, along with the nitrogen and phosphorus from waste water treatment effluent, enhanced *E. coli* recovery and regrowth (McCrary et al. in review). This research will shed light on DOC fate, source, and cycling, and will be meaningful for understanding water quality issues in Texas. The study has important local relevance as the Bryan/College Station (B/CS) region is experiencing rapid development as well as changes in land use and land cover that increase irrigation needs and may impact carbon cycling. Sound management decisions concerning irrigation water chemistry and urban development might eventually emerge to protect water quality as a result of this research.

Hypotheses

1. $H0_1$: The source of DOC in each watershed will be the same regardless of land cover and land use.

   H1: Sources of DOC will differ among watersheds according to land cover, with urban watersheds showing a greater proportion of streams with an impervious runoff and turfgrass signature as quantified with near infrared spectroscopy and carbon isotopes.

2. $H0_2$: There will be no significant differences in stream ($H0_{2a}$) or soil ($H0_{2b}$) DOC biodegradability according to different land use.
   H2: Biodegradable DOC will be higher in watersheds with less urban land use and in watersheds with waste water treatment plants due to a younger, more labile, source of DOC.
3. $H0_3$: Adsorption of DOC on soil mineral surfaces is the same regardless of land cover.
   H3: A lower proportion of input DOC will be adsorped under urban land cover due to high inputs of sodium from municipal tap water used for irrigation.

SITE DESCRIPTION

The Bryan/College Station metropolitan area in Brazos County, Texas had a population of 228,660 in 2010, compared to a population of 184,884 in 2000, an increase of approximately 19% (U.S. Census 2010; Aitkenhead-Peterson et al. 2011). The climate is classified as humid sub-tropical with an average temperature of 20°C and an average yearly precipitation of 1000 mm, which falls mostly as short, high intensity storms in the spring and fall (Aitkenhead-Peterson et al. 2011). Stream flow in dry summer months is mostly irrigation runoff in streams without a waste water treatment plant (WWTP), or irrigation runoff and effluent in streams with a WWTP (Aitkenhead-Peterson et al. 2009, 2011).

Surface water in Brazos County generally has extremely elevated concentrations of DOC, and some streams have higher mean annual DOC concentrations than any reported in the literature as of 2009 (Wolf Pen Creek: mean annual DOC of 52.5 mg/L C in 2007, with a range of 10-155 mg/L C), which may be linked to interactions with sodium in soil (Aitkenhead-Peterson et al. 2009) or the stream channel itself (Steele and Aitkenhead-Peterson 2012a). Annual mean bicarbonate concentrations in streams in the region ranged from 45-191 mg/L while sodium ranged from 32-174 mg/L in 2007 (Aitkenhead-Peterson et al. 2009). Municipal tap water also has naturally high concentrations of bicarbonate and sodium, reported at 431 mg/L and 200 mg/L respectively in a 2009 City of College Station consumer confidence report (College Station Utilities 2009). Other municipal water supplies in the study area (City of Bryan, Wellborn Special Utility District, and Wickson Creek Special Utility District) have slightly different concentrations of bicarbonate and sodium (Figure 1). Wickson Creek Special Utility District (WCSUD) has the most different municipal tap water chemistry, with relatively lower concentrations of both sodium and bicarbonate.

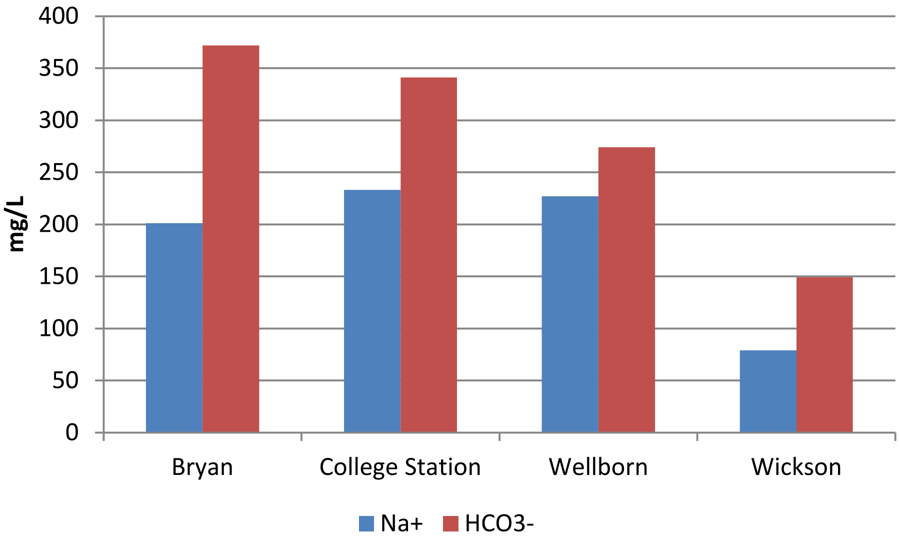

Figure 1. Chemistry of municipal tap water in the study region. Samples were obtained from between March and May 2008. Adapted from Aitkenhead-Peterson et al. 2011.

Seven watersheds in Brazos County surrounding Bryan/College Station were included in my study (Bee, Carters, Hudson, Lick, Peach, Wickson, and Wolf Pen, Figures 2 and 3). Three watersheds were considered urban with greater than 35% urban development (Bee, Hudson, and Wolf Pen), two watersheds were designated as rural with less than 35% urban development (Peach and Wickson), and two watersheds have WWTP within their basin (Carters and Lick). Land use within the seven watersheds varied from 6-100% urban, 0-35% forest, 0-16% wetland, 0-14% rangeland, and 0-63% agricultural (Table 2) as determined by the 2006 National Land Cover Data (NLCD) set published by the United States Geological Survey (USGS) in February 2011. The NLCD classification is based on the Anderson Land Cover Classification System and satellite remote sensing (Anderson 1976). Soils in the study area are mostly alfisols with marine clays and sandstone (Aitkenhead-Peterson et al. 2011). Bee, Carters, Hudson, and Wolf Pen Creeks are underlain with the Yegua formation (Aitkenhead-Peterson et al. 2011). Wickson Creek is underlain by the Cook Mountain formation, while Lick and

Peach Creeks are underlain with the Manning formation (Aitkenhead-Peterson et al. 2011).

Table 2. Percent land use in the seven study watersheds. Data is from 2006 National Land Cover Data (NLCD) published by the United States Geological Survey and calculated using Spatial Analyst in ArcGIS.

Watershed	Area km^2	Urban %	Forest	Wetland	Range	Ag-Pasture	Ag-Crop
Urban							
Bee	21.5	88.8	3.3	1.6	4.5	1.4	0
Hudson	7.6	44.1	9.2	6.9	8.6	30.5	0
Wolf Pen	6.3	100	0	0	0	0	0
Rural							
Peach	58.4	8.5	35	15.7	11.1	28.2	0
Wickson	85.0	6.0	11.3	2.1	13.0	63.2	3.7
WWTP							
Carters	57.3	69.3	5.1	4.2	6.8	12.5	1.3
Lick	46.1	32.1	23.9	7.6	14.2	21.4	0

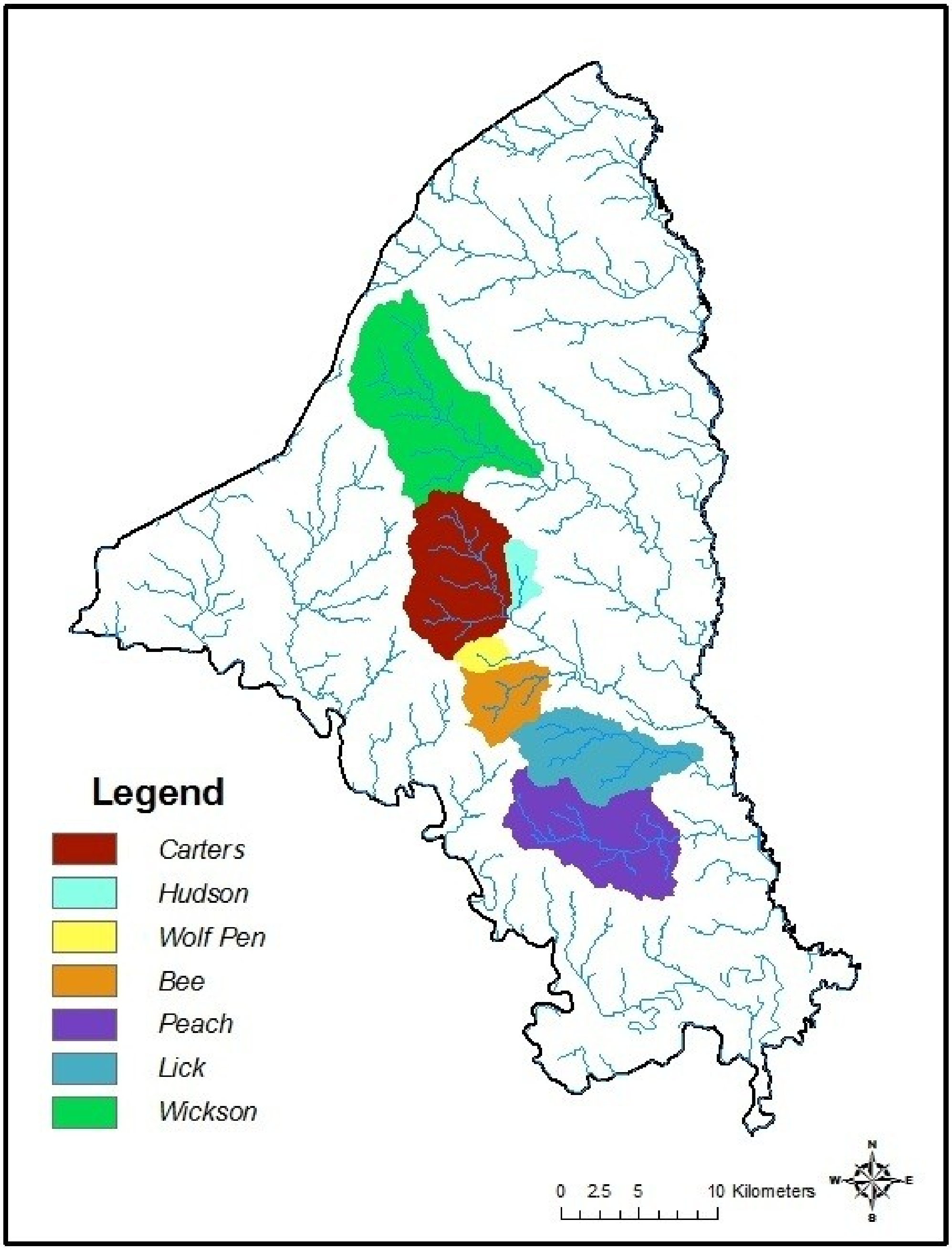

Figure 2. Study watersheds within Brazos County.

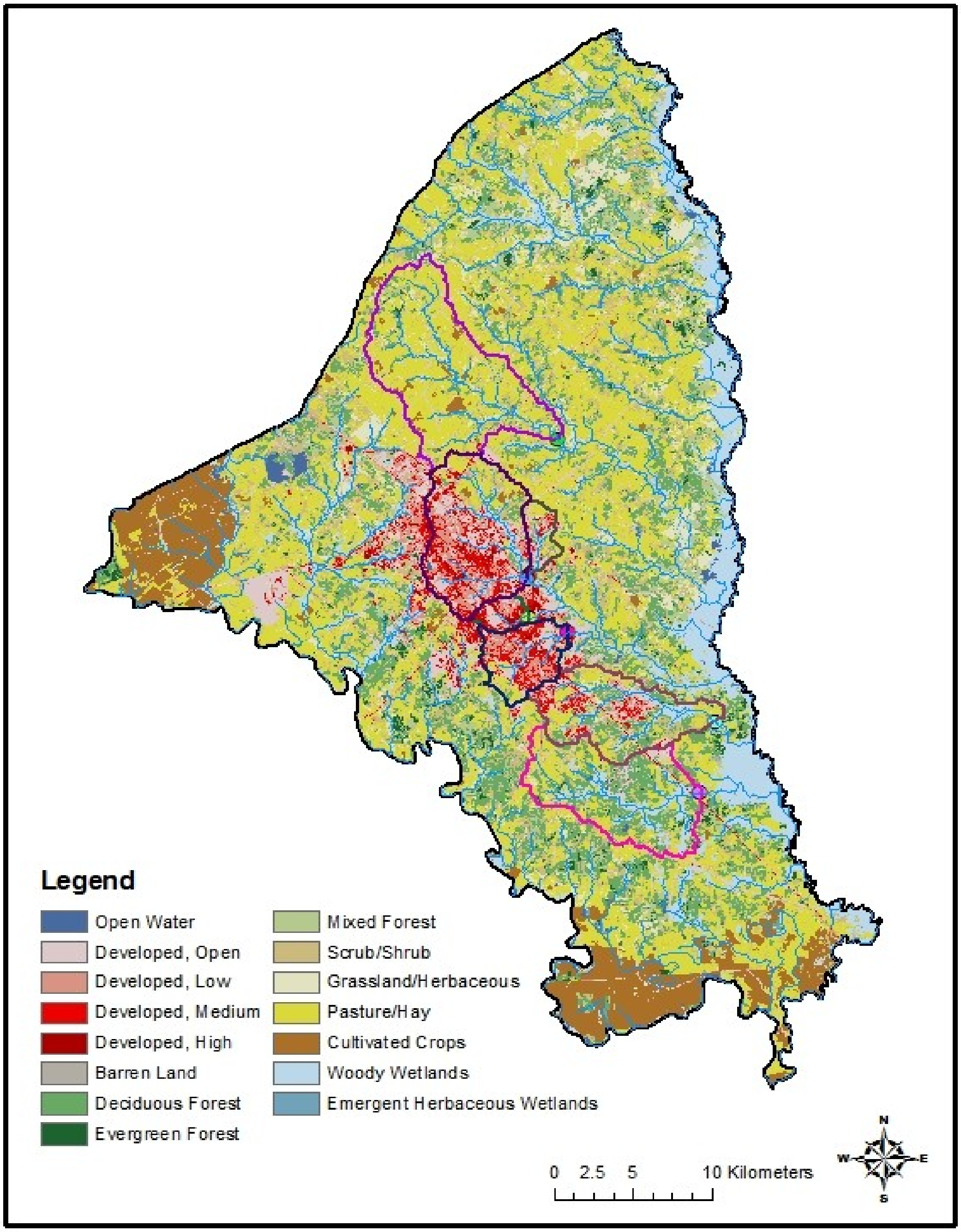

Figure 3. Land use in the study watersheds from the NLCD 2006 dataset.

Bee Creek was sampled off a bridge in a residential neighborhood on Appomattox Drive in College Station. The sampling site is located just north of Emerald Forest Park, a 4.59 acre (0.02 km^2) park dedicated to the preservation of native vegetation (City of College Station 2012a). The stream starts in Brison Park, flows through a residential area to Lemontree and Bee Creek Parks, to an open developed area, and finally to an area of forest and wetlands in Emerald Forest Park. Bee Creek meets Carters Creek approximately 1.5 km downstream. Bee Creek experienced an increase of approximately 12% urbanization from 2001 to 2006 (Fry et al. 2011).

Hudson Creek was sampled off a bridge on University Drive East/FM 60 in College Station, located northeast of the intersection with Texas State Highway 6 (SH 6). Hudson Creek's watershed is located mostly in the City of Bryan. The creek passes through Miramont Country Club, which includes a 22 hole golf course and 176 luxury residential lots ranging from 1/7 acre to greater than 1 acre (Miramont 2012). The golf course was built in 2004 and the entire complex consists of 1000 acres (4 km^2) (Miramont 2012). After Miramont, the stream passes through a small area of pasture and wetlands before crossing Boonville Road/FM 158 and entering a residential and medical complex in the Copperfield area. The stream passes through a small area of rangeland just prior to the sampling point. Hudson Creek meets Carters Creek approximately 1.5 km downstream. Hudson Creek experienced an increase of approximately 13% urbanization from 2001 to 2006 (Fry et al. 2011), which is mostly attributed to the development at Miramont.

Wolf Pen Creek was sampled from the bank of the stream just upstream of a stormwater outfall located adjacent to the parking area for Wolf Pen Creek Park off Dartmouth Street in College Station. The headwaters of Wolf Pen Creek are located just east of the 18 hole Texas A&M University golf course. The stream flows through a heavily developed residential and commercial area before entering Wolf Pen Creek Park just north of Texas Avenue South. Wolf Pen Creek was sampled midway through the park. The stream continues to pass through open developed areas and Raintree Park until its confluence with Carters Creek approximately 2.4 km downstream. There were no changes in urban land use between 2001 and 2006 as the watershed was already 100% urbanized (Fry et al. 2011).

Peach Creek was sampled off a bridge surrounded by pasture on Peach Creek Road in College Station, just downstream of where the creek crosses under SH 6. Peach Creek experienced an increase of approximately 2% urbanization from 2001 to 2006 (Fry et al. 2011). Forested land adjacent to the sampling site underwent moderate clearing for pasture towards the end of the sampling period. Peach Creek has its headwaters near the intersection of Wellborn and Barron Roads. The creek flows through mostly pasture, forest, and wetlands to its sampling point. Peach Creek drains directly into the Navasota River approximately 5 km downstream.

Wickson Creek was sampled off a bridge surrounded by pasture on Old Reliance Road in Bryan, located southeast of Texas State Highway 21 (SH 21). Wickson Creek has been listed as impaired for bacteria since 2006 according to the 2010 Texas Water Quality Integrated Report for water quality impairments as described in the Clean Water Act's 303(d) list (TCEQ 2010). This site has a category status of 5b, which indicates that a review of water quality standards will be conducted before the total maximum daily load (TMDL) process is begun (TCEQ 2010). The sampling point often had a visible oily sheen on the surface. This may be due to runoff from various industries upstream. The headwaters of Wickson Creek are located near the intersection of FM 974 and FM 2776. There has been some development of low density homes on large acreage in the headwaters, but this has not increased the urban classification since 2001. The stream flows through pasture, forest, and a small area of developed land as it crosses under SH 21. The site is sampled approximately 3.1 km downstream of SH 21. Wickson Creek continues to flow through pasture and forest until it drains directly into the Navasota River approximately 16 km downstream. Flow data collected by the Brazos River Authority between 1999 and 2004 at a site downstream of the sampling point (N=29, 18 estimates and 11 actual measurements) indicate an average flow of 13.2 cubic feet per second (cfs) (TCEQ 2012).

Carters Creek was sampled off a bridge at the northwest corner of the intersection of University Drive East/FM 60 and Texas State Highway 6 Frontage Road in College Station. Burton Creek WWTP, operated by the City of Bryan, is located on Burton Creek, which is a tributary of Carters Creek. The Burton Creek WWTP has a treatment maximum of 8.0 million gallons per day (MGD), though the plant averaged 4.76 MGD in 2010 (Figure 4, US EPA 2012a). Seven violations were reported for ammonia-N and total suspended solids (TSS) in the most recently available period (US EPA 2012a, Table 3). The sampling site for Carters Creek is downstream of the confluence of Burton and Carters Creek and approximately1.6 km downstream of the Burton Creek WWTP (Aitkenhead-Peterson et al. 2011). Carters Creek has been listed as impaired for bacteria since 1999 (TCEQ 2010). Currently, the site is listed as category 5a, which indicates that a TMDL is underway (TCEQ 2010). A draft TMDL was released for public comment in May 2012 (TWRI 2012). Carters Creek experienced an increase of approximately 2% urbanization from 2001 to 2006 (Fry et al. 2011). The headwaters of Carters Creek are near the intersection of SH 21 and SH 6. Carters Creek flows through the eastern half of the watershed, which is mostly dominated by pasture, forest, and open developed land. Several tributaries drain the urbanized western half of the watershed. Carters Creek meets the Navasota River at the north end of Sulphur Springs Road in College Station, approximately 16 km downstream of its sampling point, after continuing to flow through pasture, forest, and wetlands. Flow data collected by the Brazos River Authority between 1999 and 2004 downstream of the sampling site (N=48, 25 estimates and 23 actual measurements) indicate an average flow of 21.3 cfs (TCEQ 2012).

Lick Creek was sampled off a bridge surrounded by pasture at the northwest corner of the intersection of Peach Creek Rd and Sulphur Springs Road in College Station. This site is approximately 1.6 km downstream of the Lick Creek WWTP operated by the City of College Station (Aitkenhead-Peterson et al. 2011; College Station 2012b). The Lick Creek WWTP first came online in 1987 and currently has a treatment maximum of 2.0 MGD to serve the south side of College Station

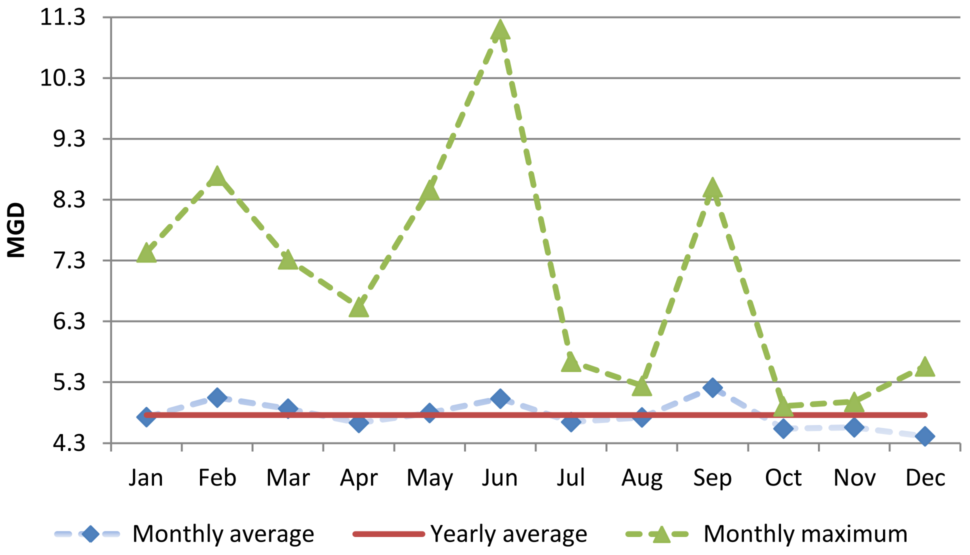

Figure 4. Average 2010 (monthly and yearly) and maximum (monthly) facility flow for Burton Creek WWTP (MGD). 2010 is the most recently available data. Data is from the U.S. EPA's Enforcment and Compliance History Online (ECHO).

Table 3. Permit violations for Lick Creek and Burton Creek WWTP in the most recently available three year period (October 2008-September 2011). Violations are expressed as the highest percentage the permit was exceeded in the given quarter. NMth= nonmonthly, a maximum amount during the quarter, Mthly= monthly, based on monthly average of readings. Data is from the U.S. EPA's Enforcment and Compliance History Online (ECHO).

		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
		Oct-Dec 08	Jan-Mar 09	Apr-Jun 09	Jul-Sep 09	Oct-Dec 09	Jan-Mar 10	Apr-Jun 10	Jul-Sep 10	Oct-Dec 10	Jan-Mar 11	Apr-Jun 11	Jul-Sep 11
Burton WWTP													
Ammonia-N	NMth					15%		79%					
Ammonia-N	Mthly							100%					
TSS	NMth								35%			40%	
TSS	Mthly									6%	5%		
Lick WWTP													
E. coli	NMth					514%		17%				514%	
TSS	Mthly				7%								

(College Station 2012; US EPA 2012b). The plant averaged 0.84 MGD in 2010 (Figure 5, US EPA 2012b). Four violations were reported for *E.coli* and TSS in the most recently available period (Table 3, USEPA 2012b). The headwaters of Lick Creek are near the intersection of Graham Road and Longmire Drive. Lick Creek flows through a developed area, under SH 6, and through a large area of forest until it meets the 36 hole golf course at Pebble Creek Country Club which also includes luxury residential development. The Pebble Creek development encompasses approximately 1,348 acres (5.5 km^2) and was built in the 1990s (Pebble Creek 2012). Lick Creek is the northern border of the development, which currently has 1,312 developed lots which average approximately 0.4 acres (0.002 km^2) in size (Mary Stephens, Brazos Central Appraisal District, personal communication, February 23, 2012). The stream continues to flow through the forested and wetland areas of Lick Creek Park and past the Lick Creek WWTP. Lick Creek flows through wetland, pasture, and forest until its confluence with the Navasota River approximately 3 km downstream of the sampling point. Lick Creek had a 2% increase in urbanization between 2001 and 2006 (Fry et al. 2006).

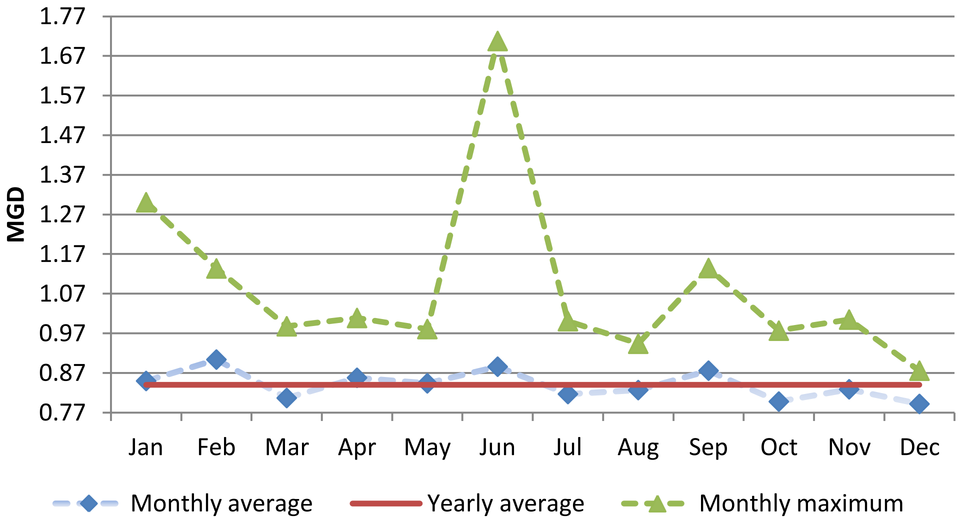

Figure 5. Average 2010 (monthly and yearly) and maximum (monthly) facility flow for Lick Creek WWTP (MGD). 2010 is the most recently available data. Data is from the U.S. EPA's Enforcment and Compliance History Online (ECHO).

MATERIALS AND METHODS

The Soil Conservation Service (SCS) Runoff Curve Number (RCN) Method

The Soil Conservation Service (SCS) created the Runoff Curve Number (RCN) Method in 1954 as an interagency tool to estimate peak runoff rates and volumes in watersheds with varying land use (Schiariti 2008). This method was used to examine runoff potential within the study watersheds. Several equations are used to determine runoff (Equations 1-4; Barfield et al. 1981; NRCS 1986). It is typically assumed that initial abstraction (I_a), or all losses before runoff begins, is equal to 20% of the potential maximum retention after runoff begins (S, Equation 2). Equation 1 can be rewritten to become Equation 3, below. The S value can be determined via Equation 3 which incorporates curve number (CN), a coefficient that represents the amount of runoff based on the type and quality of land use and land cover. Finally, runoff (Q) can be solved for after incorporating rainfall (P) in inches (Equation 4). Runoff curves can be plotted as P (rainfall, inches) versus Q (runoff, inches).

Curve number coefficients incorporate losses of precipitation to evaporation, adsorption, transpiration, and surface storage so that the higher the curve number, the greater the runoff potential (Schiariti 2008). Runoff curve numbers can be determined from Table 2.2 in Technical Release 55 (TR-55) from the United States Department of Agriculture (USDA) and Natural Resources Conservation Service (NRCS 1986). The curve numbers given in TR-55 assume average antecedent runoff condition and that I_a=0.2S. For urban areas, it is also assumed that impervious areas are directly connected to the drainage system (CN=98) and that pervious urban areas are equivalent to pasture in good hydrologic condition (NRCS 1986). Several factors influence curve number, including hydrologic soil group (HSG), hydrologic condition, cover type, and management (NRCS 1986). Soils are divided into four HSGs (A, B, C, and D) based on their minimum infiltration rate as measured for bare soil after prolonged wetting (Table 4, NRCS 1986). HSG information for the study area was obtained through soil surveys stored online through Web Soil Survey (WSS), a project of the USDA and NRCS.

Precipitation data from Easterwood Airport, College Station ("KCLL") was used for all sites except Wickson Creek, where precipitation was gathered from the Roy Ball Road station ("KTXBryan10") in Bryan (KCLL 2012; KTXBryan10 2012). Cover type and condition are used to characterize the hydraulic condition as poor, fair, or good (NRCS 1986). Hydraulic condition is further defined within the footnotes of Table 2.2 according to cover type (NRCS 1986). Hydraulic condition is replaced by average percent impervious area for urban regions.

Composite CNs for each watershed were obtained using soil survey data from WSS joined with land use and land cover data from the NLCD 2006 dataset following the example in Figure 2.5 of TR-55 (NRCS 1986). Composite CNs were calculated according to the percent of each HSG within the watershed using ArcGIS (Figures 6-8). Different land uses within the HSGs were accounted for and weighted based on percent cover. Areas reported as water were assigned a CN of 100 (Barfield et al 1981).

Table 4. Descriptions of hydrologic soil groups. Adapted from (Barfield et al. 1981; NRCS 1986).

	Group A	Group B	Group C	Group D
Soil texture	sand, loamy sand, or sandy loam	silt loam or loam	sandy clay loam	clay loam, silty clay loam, sandy clay, silty clay, or clay
Runoff potential	low	Intermediate	intermediate	High
Infiltration rate	high	Moderate	Low	very low
Water transmission	high, >0.30 in/hr	moderate, 0.15-0.30 in/hr	low, 0.05 to 0.15 in/hr	very low, 0 to 0.15 in/hr

$$Q = ((P\text{-}I_a)^2)/((P\text{-}I_a) + S)$$

where

Q= runoff (in)

P = rainfall (in)

S = potential maxiumum retention after runoff begins (in)

I_a = initial abstraction (in)

Equation (1)

$$I_a = 0.2S$$

Equation (2)

$$S = (1000/CN) \text{ -}10$$

Equation (3)

$$Q = ((P\text{-}0.2S)^2)/(P+0.8S)$$

Equation (4)

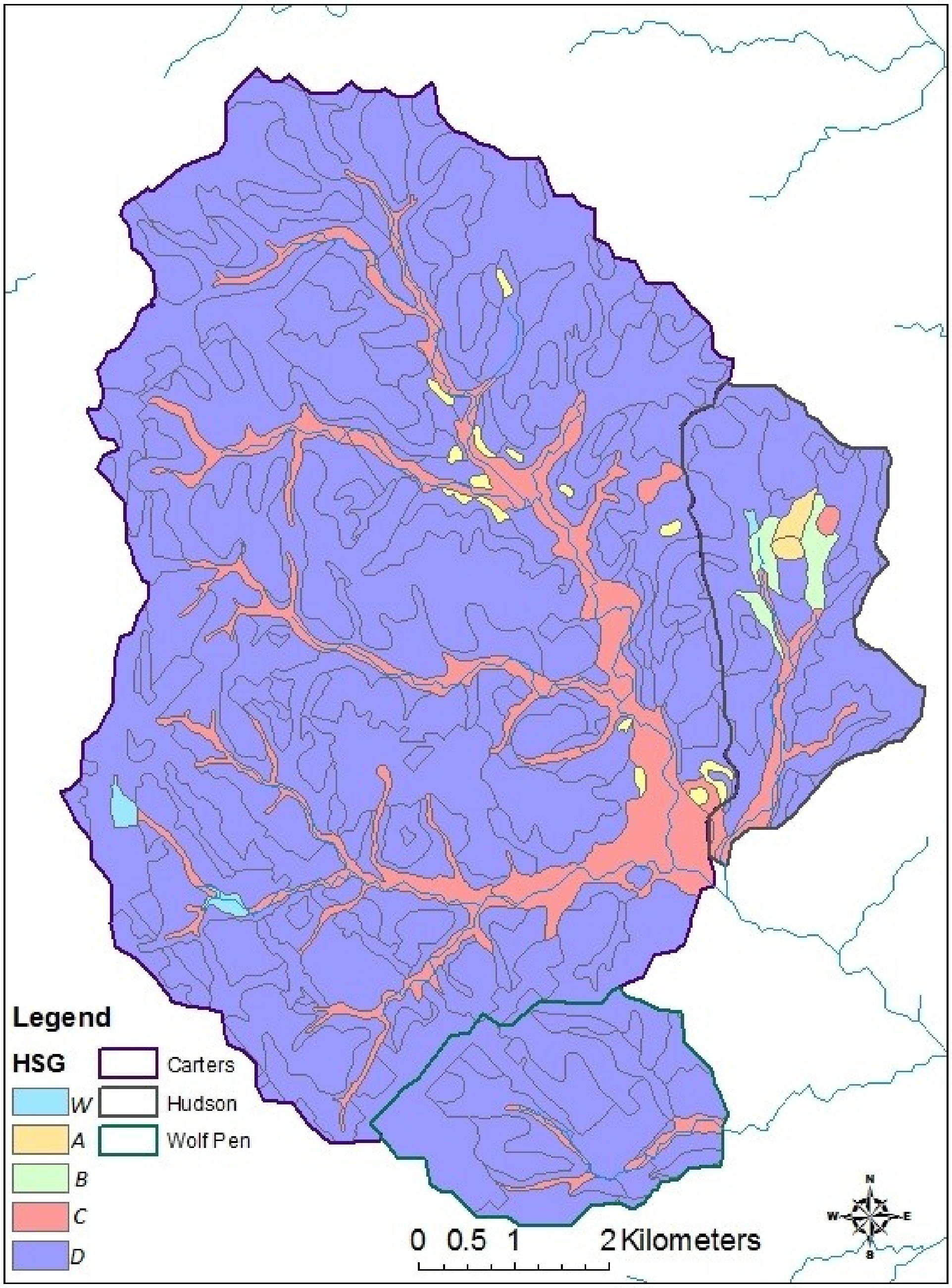

Figure 6. Map of Carters, Hudson, and Wolf Pen Creek watersheds and the soil classifications for HSG.

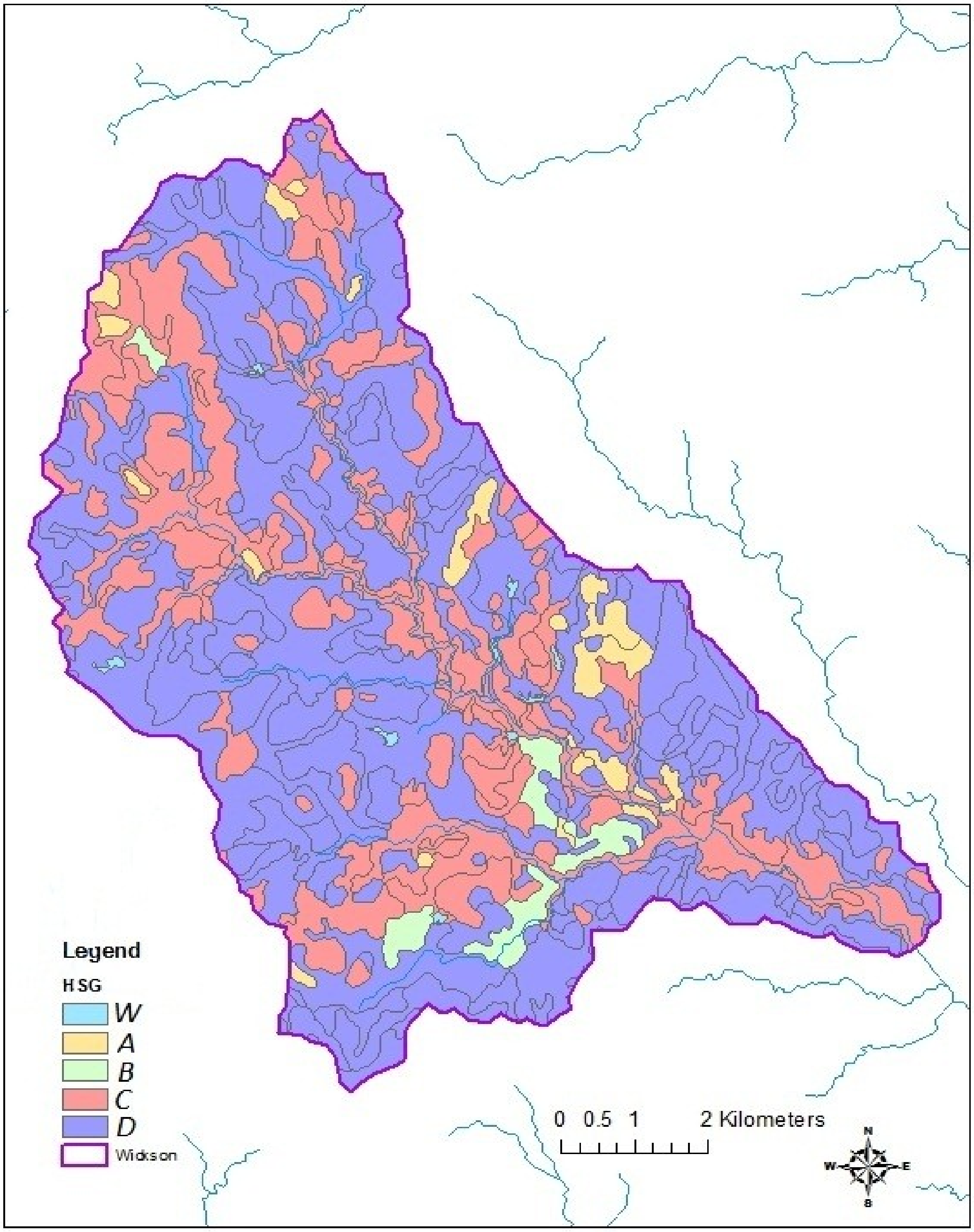

Figure 7. Map of Wickson Creek watershed and the soil classifications for HSG.

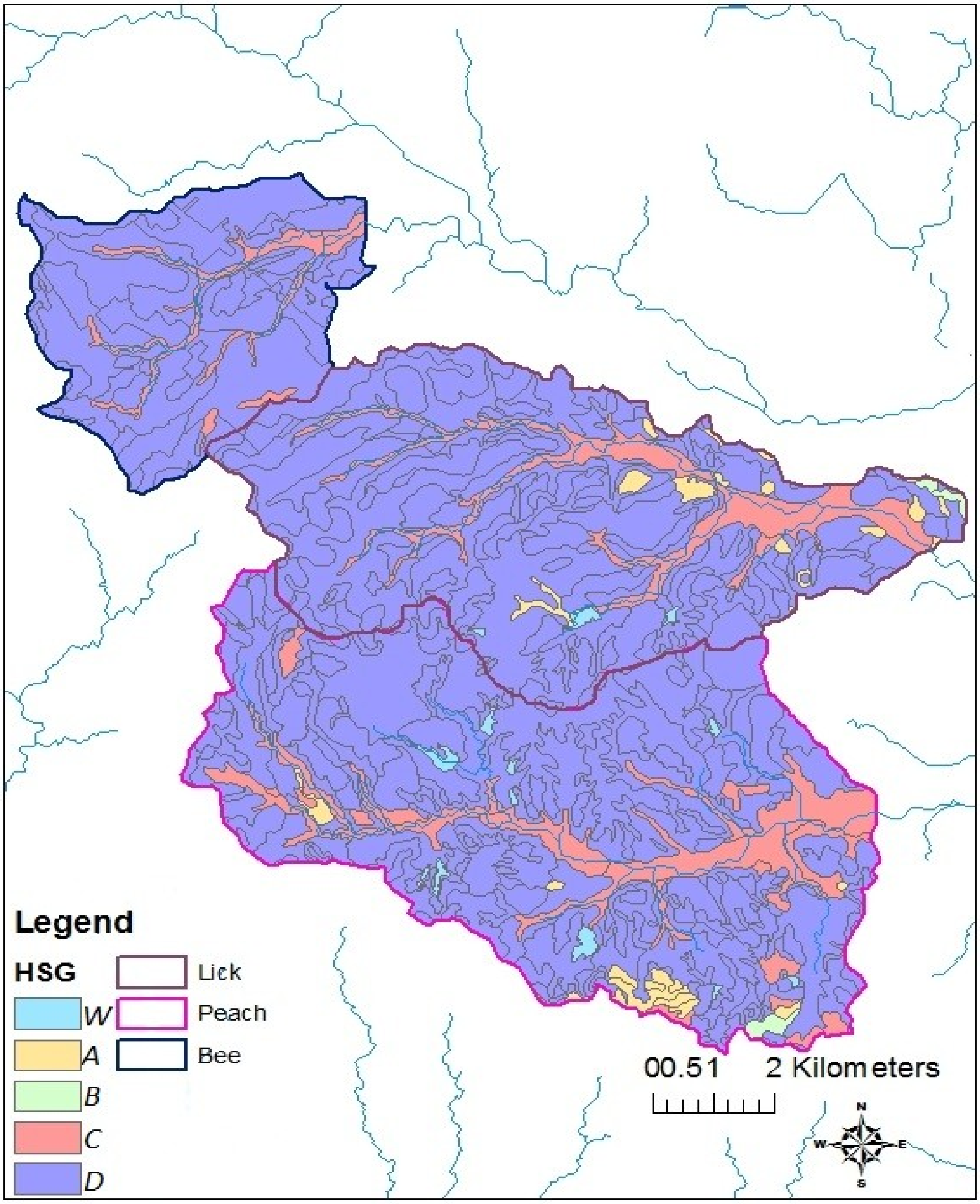

Figure 8. Map of Bee, Lick, and Peach Creek watersheds and the soil classifications for HSG.

Diffuse reflectance near infrared spectroscopy

Visible (415 to 750 nm) and near infrared (780 to 2440 nm) spectra have been analyzed with fiber optic probes and diffuse reflectance to examine organic matter source materials in various watersheds (Aitkenhead-Peterson et al. unpublished). These spectra have been combined to create a regional input database of diffuse reflectance NIR (DR-NIR) spectral signatures called the Watershed Source Spectral Library or the WSSL model (Aitkenhead-Peterson et al. unpublished). Source materials included organic matter such as WWTP effluent, fecal material from a range of animals, water extractable vegetation and soil, engine oil, and impervious runoff from different surfaces. Each source material has a unique spectral signature. The WSSL model can be used as a relatively fast and inexpensive method to source track diffuse sources of runoff to streams during all flow regimes and seasons.

25 mL aliquots of filtered stream water (nominal 0.7 μm Whatman GF/F filters) were processed using an evaporative technique to concentrate and isolate the organic compounds in the streams on a solid matrix. Stream water was added to white commercial sponges (mean diameter 57 mm, depth 10 mm, 3.017 g) and dried (50°C for 24 hours) before being scanned. A Labspec 5000 near infrared spectrometer (Analytical Spectral Devices Inc., Boulder, CO, USA) with a wavelength range from 350 to 2500 nm at a 1 nm resolution was used to take three scans of a sponge, rotating 90^0 between each new scan. Source materials were diluted in a 10:1 material: DDW solution.

The raw reflectance data was pretreated by converting to the first derivative prior to statistical analysis. Average values for each nm wavelength were calculated from the three scans of each stream sample. The average DR-NIR spectral signature of blanks (ultrapure distilled deionized water, DDW, 18.2 MΩ cm, Barnstead, on commercial sponge, n = 14) was deducted from the DR-NIR spectral signature of each of the stream samples so that only the stream material signature was considered.

Principal component analysis (PCA) was applied to the WSSL to assess clustering of sources of organic material. To remove noise at the front and back end of the spectra, PCA was run again with 350-414 nm and 2441 – 2500 nm removed from analyses. Cluster analysis (Euclidean distance using k-means clustering) was then used as a confirmation of stable clusters. Cluster analyses were performed 10 times, and each analysis had 100 iterations to reduce spatial outlier detection (SOD). Sixteen groups of source material of carbon were identified (Figure 9, Table 5). Soils divided into five groups (groups 1, 2, 10, 11 and 15), while vegetation split into two groups, with group 8 tending to have greater exposure to irrigation or irrigation runoff and group 6 consisting mainly of forest and shrub scrub vegetation. Domestic and feral animal fecal material separated into two groups (domestic, group 3 and cliff swallow, group 16) although they showed some co-correlation (Table 6). Bryan/College Station municipal tap water formed group 4, but because rural creeks in the study area have a different municipal supply with varied chemistry, group 4 is described as high $NaHCO_3$ (sodium bicarbonate) water. Pure effluent from Carters Creek WWTP split into two groups. Group 7 was made up of only effluent while group 5 included both effluent and impervious runoff. Group 12 comprised impervious runoff only. Because of the oily sheen on Wickson Creek and the potential for engine oil to be washed from impervious surfaces to streams, group 9 represents the spectra for engine oil. Groups 13 and 14 (DDW blanks and human decomposition remains) did not explain any variance in the sampled streams and were excluded from analysis.

Once the main source groups were established using PCA and cluster analysis, the average value for each 1 nm wavelength between 415 nm and 2440 nm was calculated for every source group. Regression analysis was performed between each source group and each stream collection to assess the amount of variance (R^2) that an individual WSSL source group explained of the stream spectra (Figure 10).

There was some co-correlation between groups (Table 6). In these cases, simple linear regression analysis was performed on each source group. If the R^2 value between two groups was > 0.50, then those groups were not used in the final model describing stream water content.

Table 5. Descriptions of source groups of DOM produced through the WSSL.

Group	Description
1	Soil
2	Soil
3	Domestic animal fecal material
4	High $NaHCO_3$ water
5	Effluent and impervious runoff
6	Vegetation- forest, shrub scrub
7	Effluent
8	Vegetation- irrigation exposure
9	Engine oil
10	Soil
11	Soil
12	Impervious runoff
13	Blanks
14	Human remains decomposition
15	Soil
16	Cliff swallow fecal material

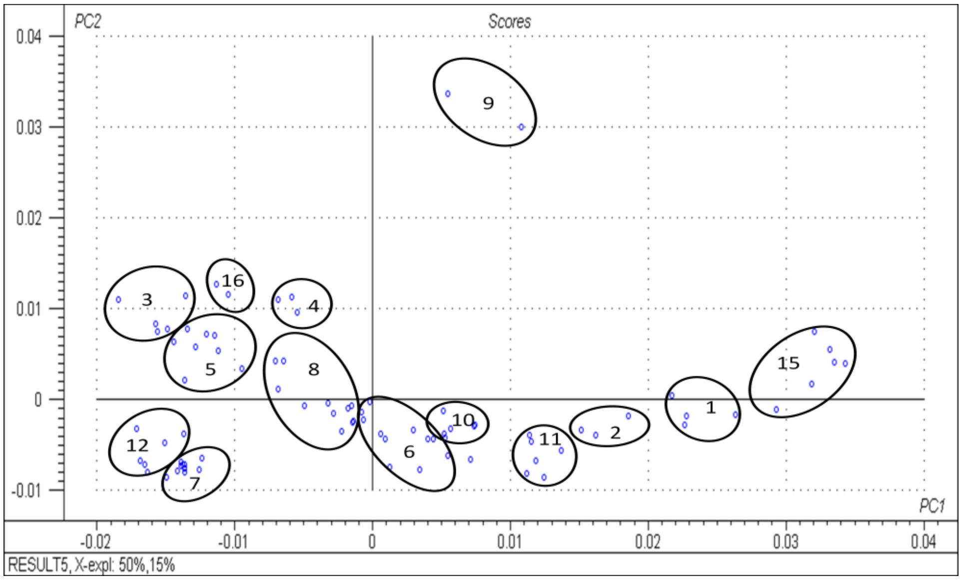

Figure 9. Principal component analysis (PCA) of spectra included in the WSSL. Groups are identified in Table 5. Groups 13 and 14 (not shown) were blanks (group 13) and human remains decomposition (group 14) and were removed from the figure as they did not explain any of the variance seen in stream spectra.

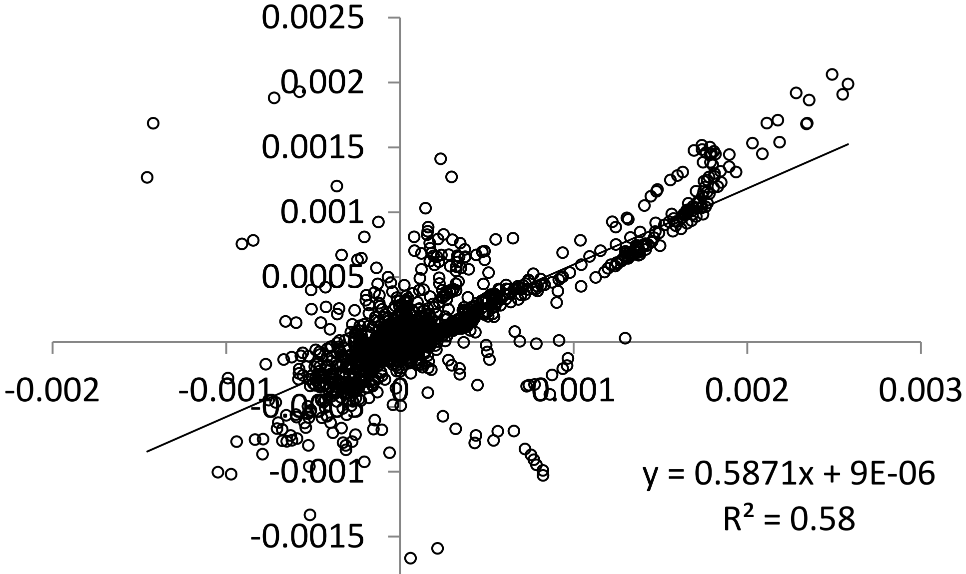

Figure 10. Example of the relationships explored between source groups and stream spectra. This figure is of the relationship between group 16 (cliff swallow feces) and Bee Creek stream water collected on 2/6/2012.

Table 6. Pearson correlations (R) among the source groups identified by cluster analysis. Bold values are not statistically different (paired t-test with equal variance; $p > 0.05$). Unbolded values are significantly different (paired t-test with equal variance; $p < 0.05$).

Group	1	2	3	4	5	6	7	8	9	10	11	12	15
1													
2	**0.97**												
3	0.06	0.18											
4	-0.08	-0.06	0.40										
5	-0.04	0.10	0.75	0.61									
6	0.57	0.71	**0.66**	0.25	0.64								
7	0.05	0.18	0.50	0.14	0.65	0.58							
8	**0.70**	**0.83**	**0.41**	0.06	0.40	0.93	**0.48**						
9	0.28	0.23	0.10	0.33	0.09	0.12	-0.13	0.05					
10	0.77	0.88	0.39	-0.03	0.34	**0.86**	**0.48**	**0.93**	0.06				
11	**0.90**	0.97	0.24	-0.11	0.16	0.78	0.33	0.9	0.13	**0.96**			
12	0.12	0.26	0.68	0.31	0.81	0.73	0.90	0.58	0	0.57	0.40		
15	**0.97**	**0.89**	0.02	-0.02	-0.09	0.44	-0.05	0.55	0.37	0.62	**0.79**	0.03	
16	0.02	0.12	0.80	**0.69**	0.82	**0.59**	0.38	0.33	0.25	0.25	0.13	0.64	-0.10

Since the sum of the amount of variance explained by sources of organic matter often exceeded 100%, and because of the high correlations between some of the groups in the WSSL, three models (urban, rural, and WWTP) were constructed (Table 7). Each model was based on land use and known inputs to the stream. The goal was to select groups that could explain up to 100% of the variance in stream water but were not correlated to each other.

Vegetation groups used in each model were chosen based on land use characteristics and can be considered subjective in the development of this preliminary model. Group 8 was selected for the urban watersheds because the vegetation in this group was dominated by irrigated lawns. Comparatively, group 6 vegetation was chosen for the rural and WWTP models. Soil was selected based on sampling location, as well as a low correlation between the vegetation and the soil groups. Spectra of engine oil and $NaHCO_3$ water were not correlated with any group and were therefore used in all three models. Cliff swallow fecal material was used in the urban model due to the prevalence of the birds in urban environments. Domestic animal fecal material was included in the rural model because the source material included fecal samples from animals (chicken, cow, dog, and pigeon) that are common in the rural communities in the region. Fecal material was highly correlated with runoff (group 5), therefore both fecal material and runoff could not be used in the same model. For the WWTP model, the logical group to include was effluent (group 7). However, the effluent group (7) was highly correlated to runoff, which may have included fecal material from domestic animals.

Table 7. Models used to describe the relative contribution of each source material to DOM in stream water.

		Land use model		
Group	Description	Urban	Rural	WTTP
1, 2, 10, 11, 15	Soil	15	1	11
6, 8	Vegetation	8	6	6
3, 16	Feces	16	3	-
7	Effluent	-	-	7
5	Effluent + Runoff	-	-	-
12	Runoff	-	-	-
4	High $NaHCO_3$ water	4	4	4
9	Engine oil	9	9	9

Isotope analysis

A subset of 32 samples out of the 87 collected stream water samples (Table 8) were evaporated to dryness using freeze dryers at the Geochemical and Environmental Research Group (GERG) of Texas A&M University and the solid residue (~1 mg C) was recovered (Gandhi et al. 2004). Subsamples of the dried residues were weighed into silver capsules using a microbalance and treated with HCl vapor in a desiccator to volatilize inorganic C present as $CaCO_3$ (Harris et al. 2001). Finally, samples were analyzed for $\delta^{13}C$ using a Carlo Erba EA-1108 (CE Elantech, Lakewood, NJ, USA) interfaced with a Delta Plus (ThermoFinnigan, San Jose, CA, USA) isotope ratio mass spectrometer operating in continuous flow mode (Boutton et al. 2009). Samples were prepared and analyzed at the Stable Isotopes for Biosphere Science (SIBS) Laboratory, Texas A&M University, under the direction of Dr. Thomas Boutton. Carbon isotope ratios are presented in δ-notation shown below in Equation 5 where R_{sample} is the $^{13}C/^{12}C$ ratio of the sample and R_{std} is the $^{13}C/^{12}C$ ratio of the Vienna Pee Dee Belemnite (V-PDB) standard (Coplen 1996).

$$\delta^{13}C = [(R_{sample} - R_{std})/R_{std}] * 10^3$$

Equation (5)

Isotope data were compared to data from DR-NIR spectroscopy in order to confirm dominant DOC source as from C_3 or C_4 vegetation.

DOC biodegradability in streams

The seven study watersheds were sampled monthly to examine biodegradability of DOC in surface water. Stream samples were collected from March 2011- February 2012. Approximately 25% of samples were taken during rain events to capture the influence of stormwater runoff within the watersheds. Rain event samples are denoted with an asterisk in figures in this thesis. Stream water samples were collected in sterile 500 mL Nasco Whirlpak bags and transported back to the Nutrient and Water Analysis (NAWA) Research Laboratory, Texas A&M University, for biodegradability analysis. Electrical conductivity (EC, VWR 89094-958) and pH (Beckmann 255) were recorded on unfiltered samples. Stream water samples were then filtered through nominal 1.2 µm Fisher GF/F filters, followed by a second filtration through nominal 0.7 µm Whatman GF/F filters, and frozen until analysis for all other chemical parameters.

Biodegradation of DOC was based on the 7 day incubation method of McDowell et al. (2006) at 25°C. 70 mL of the stream water sample was inoculated with 10 mL of WWTP effluent. Effluent was collected from the Carters Creek WWTP in College Station after all treatment stages but before UV disinfection. Effluent was collected each month just prior to biodegradability incubations and was stored at 4°C in 500mL HDPE bottles until needed. A nutrient mixture (2 mL), with concentrations of 1.82 mM nitrogen, 2.43 mM phosphorus, 0.070 mM sulfur, and 2.42 mM potassium, was added to create ideal conditions for DOC biodegradation by microbes (McDowell et al. 2006). Three small pieces of an ashed Fisher GF/F 1.2 µm filter was added to act as substrate for microbes (Qualls and Haines 1992). Filled incubation flasks were sealed with parafilm prior to incubation to prevent evaporation. Samples were run in triplicate and analyzed at time (t) 0 days and 7 days. To assess DOC at t=0 and t=7, mass of DOC in the sample and inoculant was calculated as shown in Equations 6 and 7. Biodegradable dissolved organic carbon was calculated as shown in Equation 8.

Table 8. Stream samples collected during sampling period March 2011-February 2012. A non sampling date indicates the site was dry. Rain values are from Easterwood Airport, reported in inches, for the time period prior to sampling. Asterisks indicate rain event.

Sampling date	Rain	Isotope analysis	Bee	Carters	Hudson	Lick	Peach	Wickson	Wolf Pen
3/4/2011			x	x	x	x	x	x	x
4/11/2011		x	x	x	x	x		x	x
5/13/2011*	1.88" 48 hrs		x	x	x	x		x	x
6/08/2011			x	x	x	x		x	x
6/22/2011*	2.45" 24 hrs	x	x	x	x	x	x	x	x
7/1/2011			x	x	x	x		x	x
8/2/2011			x	x	x	x		x	x
9/6/2011		x	x	x	x	x		x	x
9/19/2011*	1.4" 24 hrs		x	x	x	x		x	x
10/5/2011			x	x	x	x			x
11/10/2011		x	x	x	x	x		x	x
12/3/2011			x	x	x	x		x	x
1/16/2012		x	x	x	x	x	x	x	x
2/6/2012*	6.27" 72 hrs		x	x	x	x	x	x	x

$$DOC_{m0} = \mathit{Sample\ Xmg/L}/1000*70\text{mL} + \mathit{Inoculant\ Xmg/L}/1000*10\text{mL}$$

Equation (6)

$$DOC_{m7} = \mathit{Sample\ Xmg/L}/1000*82\text{mL}$$

Equation (7)

%BDOC was calculated as:

$$DOC_{m0} - DOC_{m7}/DOC_{m0}*100$$

Equation (8)

Two controls were used in my study. A 25 mg/L D (+) anhydrous glucose solution was used to assess microbial uptake, and a second control of DDW was used as a blank. Both controls were spiked with 10 mL effluent inoculant and 2 mL of the prepared nutrient solution. BDOC over 90% in the glucose control indicated that inoculant microbes successfully used the DOC available in solution.

DOC biodegradability in soil extracts

Soil in the study area was sampled according to land use classification following the categorization used by the 2006 National Land Cover Data (NLCD) set published by the United States Geological Survey (USGS) in February 2011. The NLCD classification is based on the Anderson Land Cover Classification System and satellite remote sensing (Anderson 1976). Samples were taken in triplicate for the following 8 land uses, for a total of 24 soil samples: 1) developed open space, 2) developed low intensity, 3) developed medium intensity, 4) developed high intensity, 5) forest, 6) pasture, 7) wetlands, and 8) rangeland/shrub scrub. Soils were collected on multiple sampling dates including June 2011, October 2011, November 2011, and January 2012 (Figure 11). Soil was sampled to a depth of 15cm in the different land uses and stored in plastic bags until drying and processing occurred.

Soil was air-dried and then sieved (2 mm) to remove stones and roots. 9.0 g of soil was combined with 90 mL DDW and shaken at 50 rpm for 4 hours. The soil and water mixture was centrifuged (Sorvall RC6 Plus) at 10,000 g-force for 15 minutes. Supernatant was removed and pH and EC were recorded prior to syringe filtration through a nominal 0.7 µm Whatman GF/F filter. Soils were run in triplicate for each site and bulked to allow for sufficient solution to run replicates for biodegradability. Approximately 75 mL of extract solution was available from each sample after centrifuging. The volume of bulked extract was recorded. An aliquot from the bulked solution was removed to quantify DOC concentration so that solutions for the biodegradability experiment could be diluted to achieve 20 mg/L DOC. Typically DOC in soil solution for biodegradability studies should be between 10 and 30 mg/L

(McDowell et al. 2006). Biodegradability analysis followed the method described above for stream water.

DOC biodegradability in vegetation extracts

Above-ground vegetation was collected with each soil sample and stored in paper bags. The vegetation was dried at 50°C in an oven for 7 days. 24 g of vegetation from each site was combined with 960 mL of DDW and was soaked for 48 hours, stirring daily. A 40:1 water to vegetation ratio for a stock solution was produced from this process. The solution was centrifuged at 10,000 g-force for 15 minutes and filtered through nominal 0.7 µm Whatman GF/F filters. An aliquot of the solution was removed to quantify DOC concentration so that solutions for the biodegradability experiment can be diluted to 20 mg/L DOC. Biodegradability analysis followed the method described above for stream water.

Soil adsorption

Seven standard solutions, diluted to range from 0 to 200 mg/L of the DOC vegetation stock concentration, were prepared in 100 mL volumetric flasks. Duplicates were run for each soil:vegetation combination. 3.0 g of sieved soil were combined with 30 mL of input solution at a 1:10 soil:solution ratio in HDPE centrifuge tubes. Following a slightly modified method of Nodvin et al. (1986), the soil/solution units were shaken at 50 rpm for 20 hours at 20°C prior to centrifugation at 10,000 g-force for 15 minutes. The supernatant was removed and pH and EC were recorded. Supernatant was then syringe filtered through nominal 0.7 µm Whatman GF/F filters prior to DOC analysis.

Retention or release of DOC was analyzed using the initial mass (IM) isotherm as described by Nodvin et al. (1986). This method has been widely used for the characterization of DOC sorption in soils (Guggenberger and Zech 1992; Moore et al. 1992; Vance and David 1992; Donald et al. 1993; Riffaldi et al. 1998). In the IM approach, the mass of a substance retained or released (RE, mg/kg) is the product of input mass (X_i, mg/kg) minus output mass (X_f, mg/kg) based on the initial and final solution concentrations of a substance (C_i and C_f, mg/L). RE was plotted against the

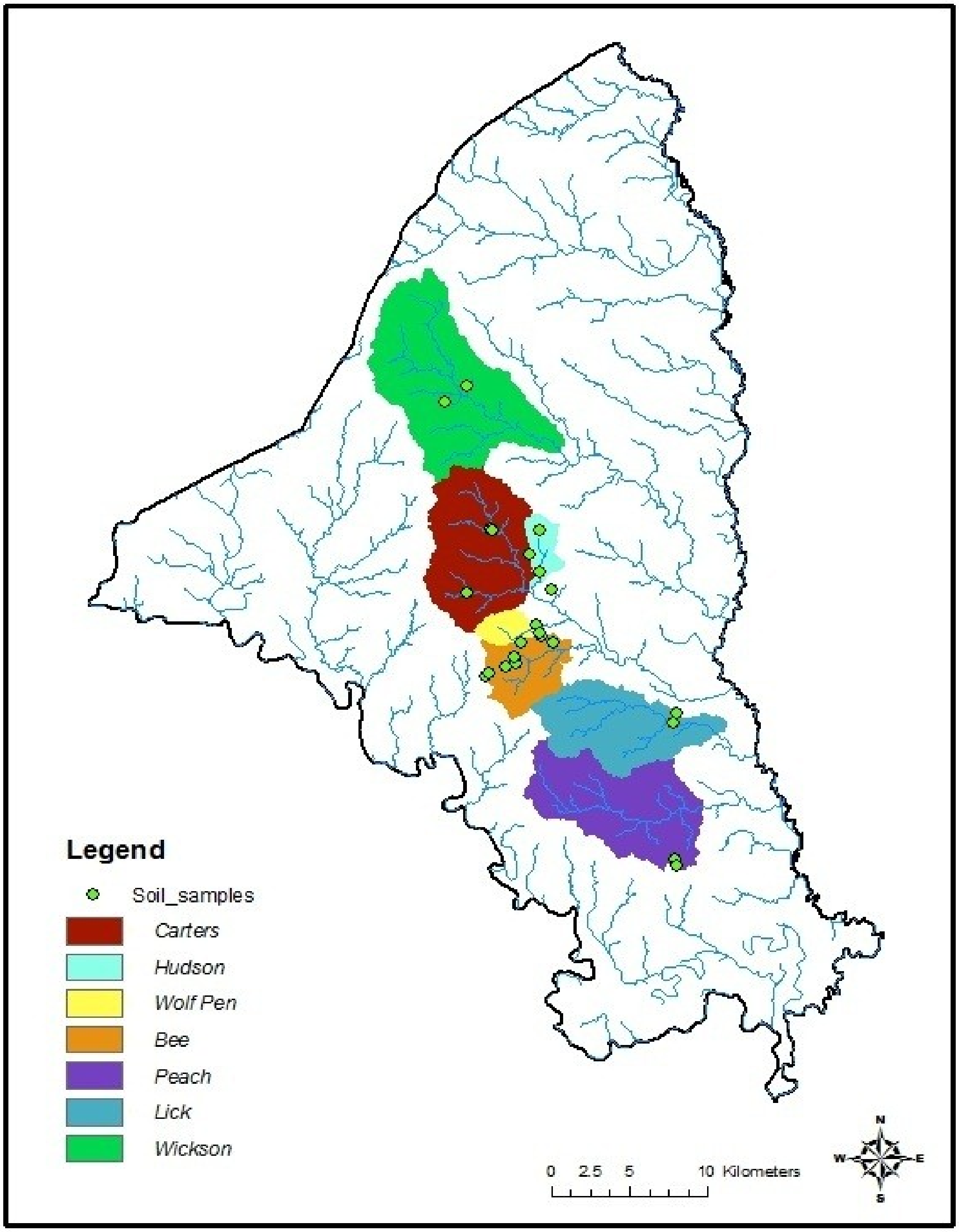

Figure 11. Soil and vegetation sample locations within watershed study area.

initial mass of the substance added and normalized to soil mass X_i to obtain both an adsorption coefficient (m, unitless) and a release term (b) as shown in Equation 9.

$$RE = mX_i - b$$

Equation (9)

The slope of the linear regression (m) gives a measure for the affinity of the substance to the sorbent (adsorption coefficient). The intercept of the equation (b, mg/kg) indicates the amount of substance released from the soil when a solution with a zero sorbate concentration is added. The calculations for the samples were performed on a dry weight basis. Reactive soil pool (RSP, mg/kg), a measure of the amount of DOC that is likely to be leached from soil (Neff and Asner 2001), was also calculated as described in Equation 10 (Nodvin et al. 1986).

$$RSP = b/(1\text{-}m)$$

Equation (10)

Soil extracts were analyzed for base cations and calcium, magnesium, and sodium were used to determine sodium adsorption ratio (SAR) after conversion of ion concentrations from mg/L to meq/L (Equation 11). Sodium adsorption ratio examines the ratio of a harmful element (sodium) to beneficial elements (calcium and magnesium) in a soil (Munshower 1994). It can also be used to determine irrigation water quality. Soil problems typically occur when SAR reaches 12-15 and vegetation is less likely to take up water (Munshower 1994). However, recent work in Texas found that an SAR of less than 5 was conducive to the release of DOC from soil (Steele and Aitkenhead-Peterson 2012b).

$$SAR = [Na^{+}]/((Ca^{2+}) + (Mg^{2+})/2)^{0.5}$$

Equation (11)

Chemical analysis

Dissolved organic carbon was quantified using high temperature Platinum-catalyzed combustion with a Shimadzu TOC-VCSH and Shimadzu total measuring unit TNM-1 (Shimadzu Corp. Houston, Texas, USA). Dissolved organic carbon was measured as non-purgeable carbon which entails acidifying the sample (250 µL, 2M HCl) and sparging for 4 minutes with carbon free air. Calcium, magnesium, potassium, and sodium were quantified by ion chromatography using an Ionpac CS16 analytical and Ionpac GC16 guard column for separation and 20mM methanosulfonic acid as eluent at a flow rate of 1mL/minute and an injection volume of 10µL with a Dionex ICS 1000 (Dionex Corp. Sunnyvale, California, USA). National Institute of Standards and Technology (NIST) traceable reference materials, replicate standards, and replicate samples were run every tenth sample to monitor instrument precision.

Statistical analysis

Diffuse reflectance near infrared spectroscopy

Principal component analysis and cluster analysis with Euclidean distance was performed using Unscrambler v. 9.8: chemometric software. Regression analyses between cluster groups and stream spectra were performed using Microsoft Excel 2007. Partial least squares regression in Unscrambler was used to examine the relationship between stream spectra and carbon isotope values.

Isotope analysis

Isotope data were analyzed using a one way analysis of variance (ANOVA) by stream and land use with a post-hoc Tukey test in SPSS Version 16.0 to determine if there was any significant difference in carbon isotope values.

Stream water chemistry

Annual and seasonal means of stream DOC were calculated. Winter was defined as December, January, and February and the remaining seasons were each three month period thereafter. A one way ANOVA by sampling site and a post-hoc Tukey test was used to determine any significant differences among parameters.

Stream biodegradability

To determine if there was any significant difference in source and biodegradability of stream DOC, a one way ANOVA by sampling site and a post-hoc Tukey test was used.

Soil biodegradability and soil adsorption

A one way ANOVA with a post-hoc Tukey test was used with land use as the independent variable to examine if land use had an effect on DOC fate, such as soil extract biodegradability and adsorption to mineral soil. To examine significant differences in soil extract biodegradability and soil retention or release of DOC, two sample two tailed t-tests were used. Backward multiple regression analysis was used to explore relationships between adsorption and soil chemistry terms.

Synthesis of sources and fates of DOC

Pearson bivariate correlation was used to determine any significant relationships between water, soil, and vegetation chemistry, and land use.

Spatial analysis

ArcGIS Desktop ESRI ArcMap 9.3.1 was used to conduct all spatial analysis. Watershed delineation was performed and overlaid on USGS NLCD 2006 data to examine land use. Area of each land use was estimated by using the Spatial Analyst tool in ArcView. These resulting areas were divided by total watershed area to determine the percent of each land use within the watershed. Area of each HSG was determined using the Spatial Analyst tool for SCS curve number analysis. Land use was calculated for each HSG to determine composite curve numbers. All analysis was conducted under the Universal Transverse Mercator (UTM) projection referenced to the North American Datum 1983 (NAD83).

RESULTS

The Soil Conservation Service (SCS) Runoff Curve Number (RCN) Method

The RCN Method showed that the greatest direct runoff would be at two urban sites and one WWTP site (Wolf Pen, Bee, and Carters Creeks), followed by Hudson (an urban site) and Lick Creeks (a rural WWTP site), and finally Wickson and Peach Creeks, rural sites (Figure 12). Figure 13 is the same data, but does not include the large rain event in February 2012 order to show more detail in the lower range of precipitation values. The RCN Method supports the fact that there will be greater runoff at more urbanized watersheds due to an increase in impervious surfaces (Hook and Yeakley 2005).

Sources of dissolved organic carbon in rural and urban watersheds

Diffuse reflectance near infrared spectroscopy

To examine the relative contribution of watershed source materials, data were plotted as a 100% stacked bar chart for each stream (Figures 14-16). All urban sites showed a large contribution from cliff swallow feces (Figure 14). The June 2 rain event showed increased influences of soil and vegetation in urban streams. High $NaHCO_3$ tap water was seen in every urban sample. Peach Creek, a rural site, was dominated by effluent and runoff (Figure 15). However, this site was dry for most of the sampling period and only had 4 samples taken compared to 14 samples at other sites. Soil was more influential at Wickson Creek than any other site. Samples with an increased signature of $NaHCO_3$ tap water in Wickson Creek tended to have a decreased signature of soil. Streams with a WWTP showed the signature of effluent and runoff, as well as feces (Figure 16).

Analysis of stream spectra using the urban, rural, and WWTP WSSL models revealed that the amount of variance explained by the spectra varied between watersheds and sampling date. The summed amount of variance explained by each model ranged from 10% to 150% (R^2 0.1-1.5; Figures 17-19). The WSSL model was not able to explain most of the variance at Peach and Wickson Creeks (Figure 18).

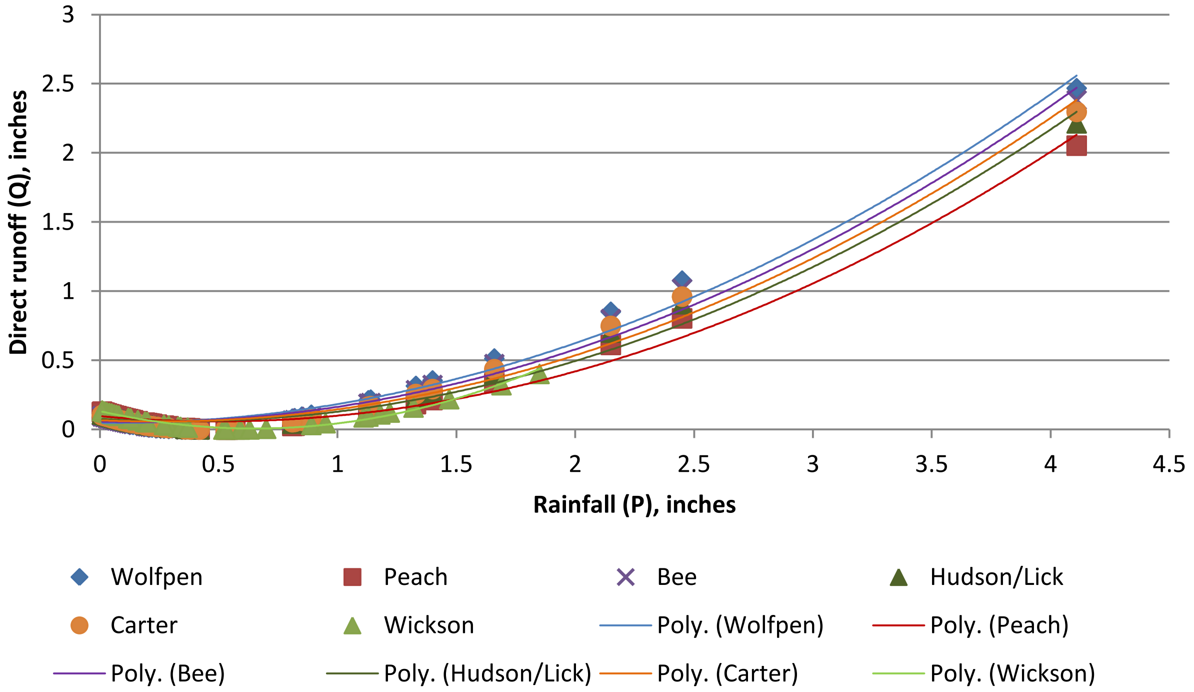

Figure 12. Results of SCS CN runoff model.

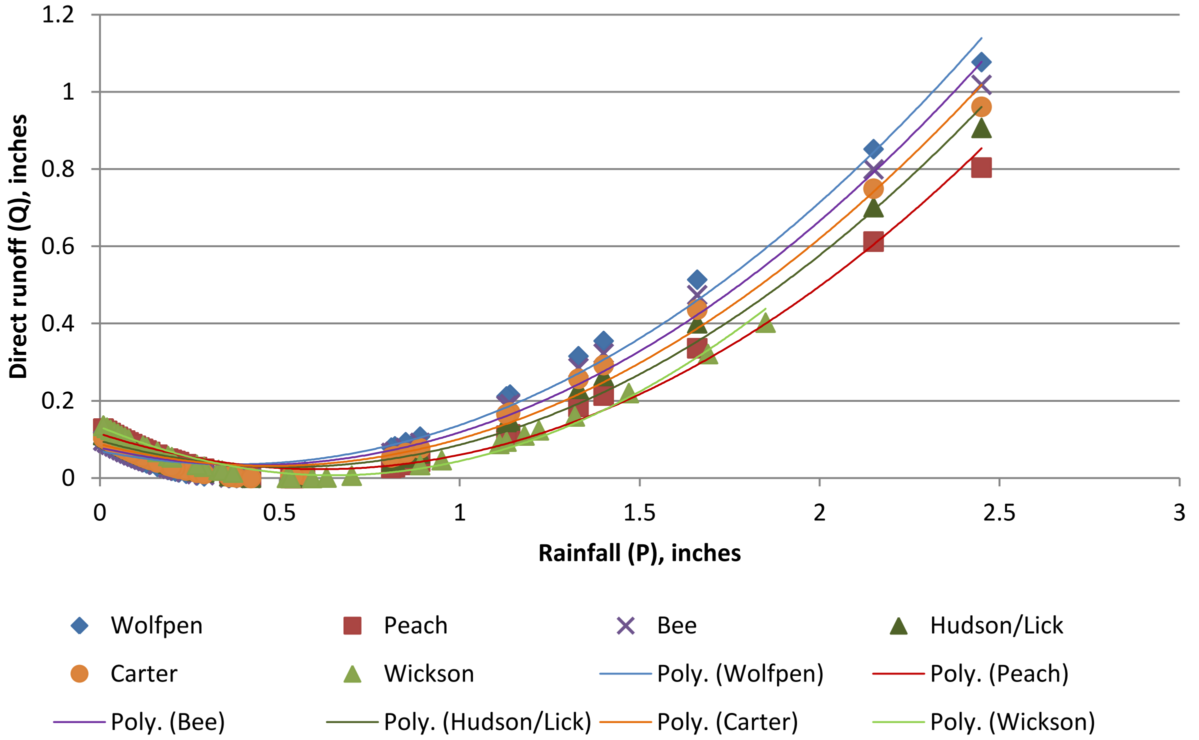

Figure 13. Results of SCS CN runoff model with large rain event (4”+) removed.

The amount of variance in stream spectra explained by soil varied between the study streams. For the urban streams, soil explained between 0 and 9% of the variance in stream spectra at Wolf Pen Creek, 0 to 4% at Bee Creek, and 0 to 6% at Hudson Creek. In the rural sites, 0 to 22% of the variance in stream spectra was explained by soil at Wickson Creek. Peach Creek did not have a measurable contribution from soil. Explained variance ranged from 0 to 28% at Carters Creek and 0 to 42% at Lick Creek, both of which had a WWTP upstream of the sampling point.

Vegetation explained a considerable proportion of the variance in stream spectra in all sampled streams. In the urban streams, vegetation explained between 0 and 27% in Wolf Pen Creek, 2 and 29% in Bee Creek, and 1 and 39% in Hudson Creek stream spectra. At the rural sites, up to 37% of the variance in stream spectra was explained by vegetation in Wickson Creek, while only up to 11% of the variance in stream spectra was explained by vegetation in Peach Creek. In the watersheds with a WWTP, the amount of variance explained by vegetation ranged from 1 to 57% in Carters Creek and between 2 and 55% in Lick Creek.

Fecal contributions within each WSSL model were different according to the source group used. Feces from cliff swallows were selected for the urban model due to their prevalence (assumed by number of nests) under bridges, on commercial buildings, and homes. Between 5 and 70% of the variance in stream spectra was explained by cliff swallow feces at Wolf Pen Creek, 31 and 82% at Hudson Creek, and 18 and 73% at Bee Creek. Feces from domesticated animals (chickens, cows, dogs, and pigeons) were used for the rural WSSL model. Between 1 and 46% of the variance in stream spectra was explained by domestic animal feces for Wickson Creek, and between 14 and 33% of the variance was explained for Peach Creek. For the WWTP sites, effluent explained between 0 and 56% of the variance in stream spectra at Carters Creek and between 9 and 30% of the variance in stream spectra at Lick Creek.

Water with a high concentration of $NaHCO_3$ was included in each model because it was not highly correlated to any other group, with the exception of cliff swallow feces. This correlation is likely because feces were collected in a small bucket resting below a

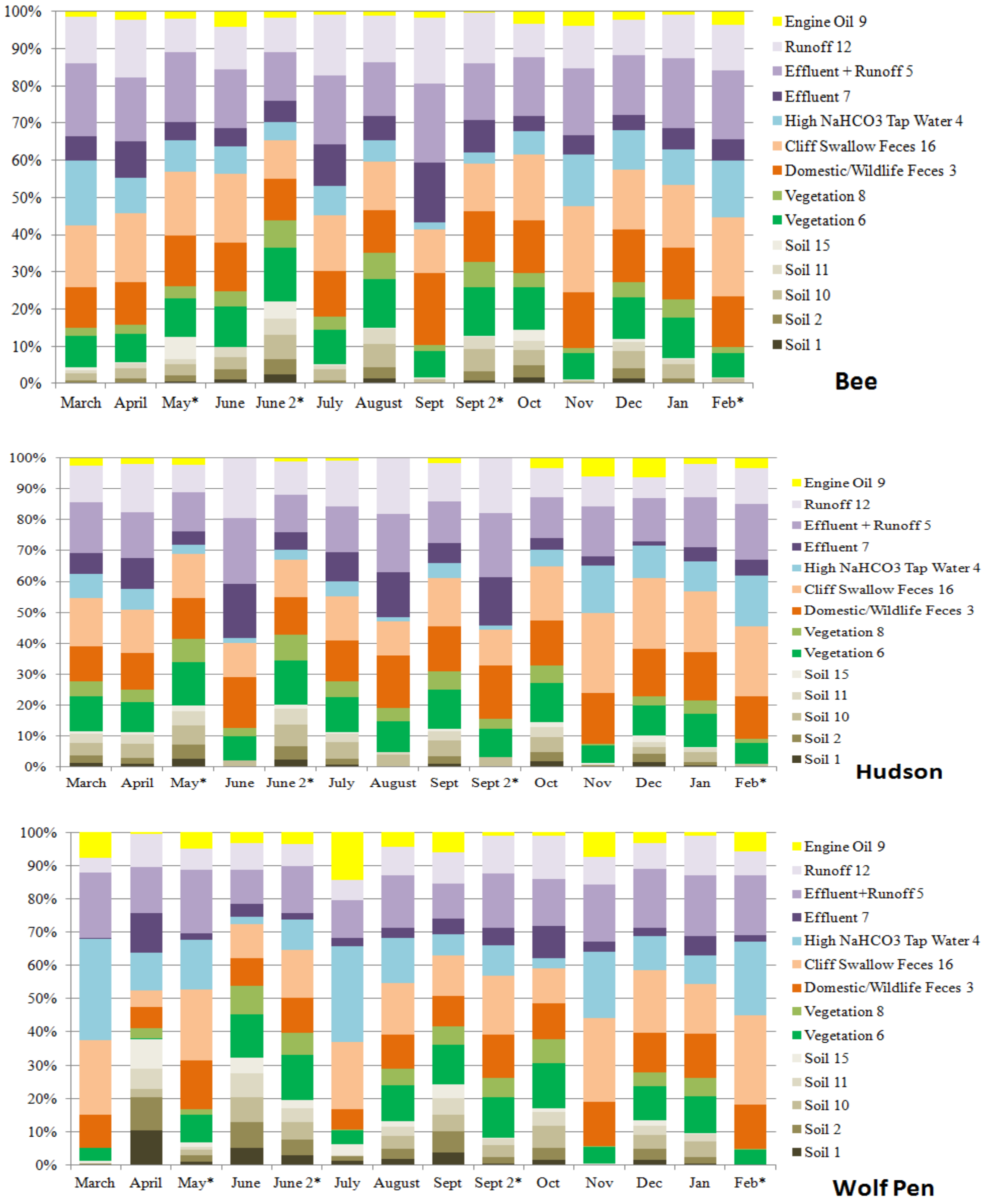

Figure 14. Relative contribution of DOM source material on each sampling date based on stream spectra at urban sites. Asterisks indicate rain event.

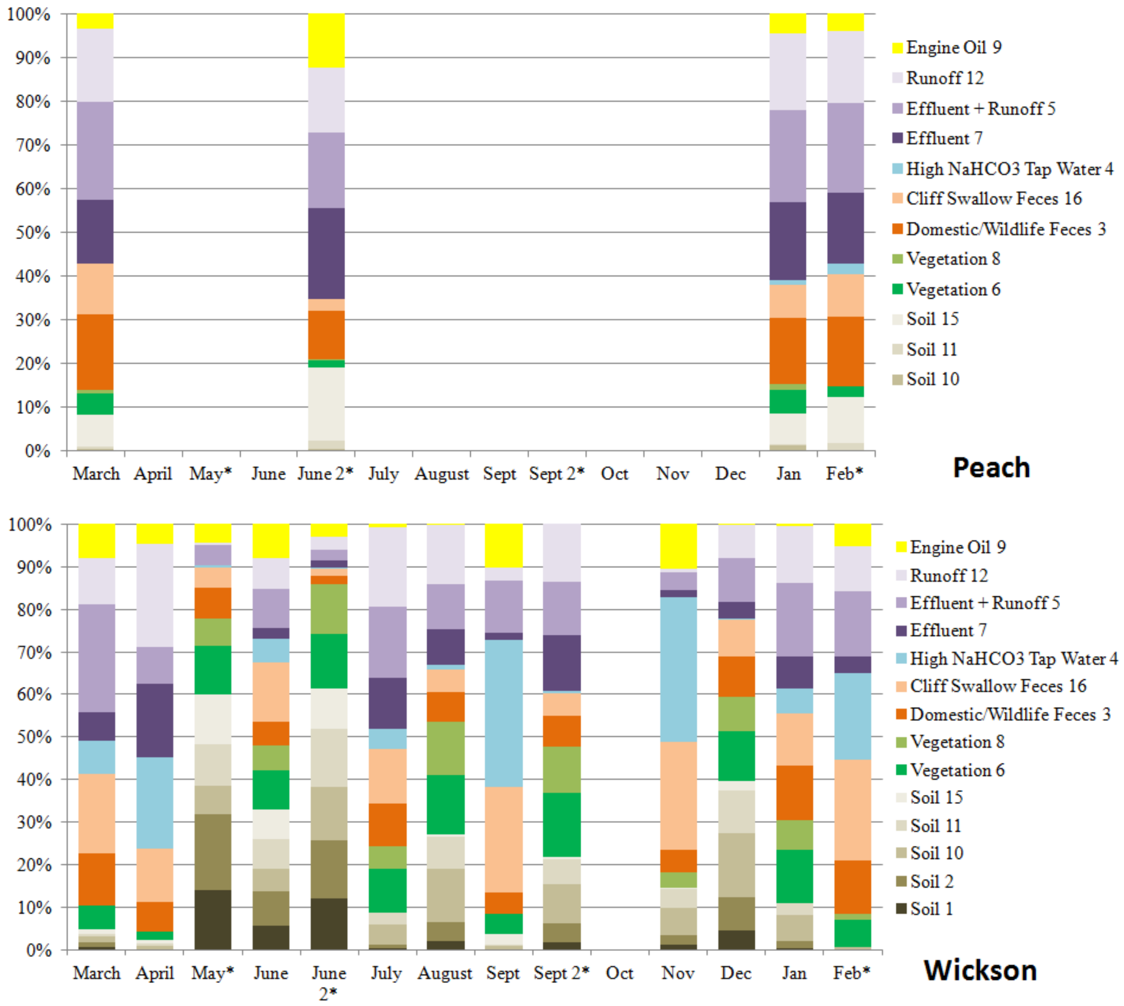

Figure 15. Relative contribution of DOM source material on each sampling date based on stream spectra at rural sites. Asterisks indicate rain event. Peach Creek was dry during 10 of the sampling dates. Wickson Creek was during one sampling date.

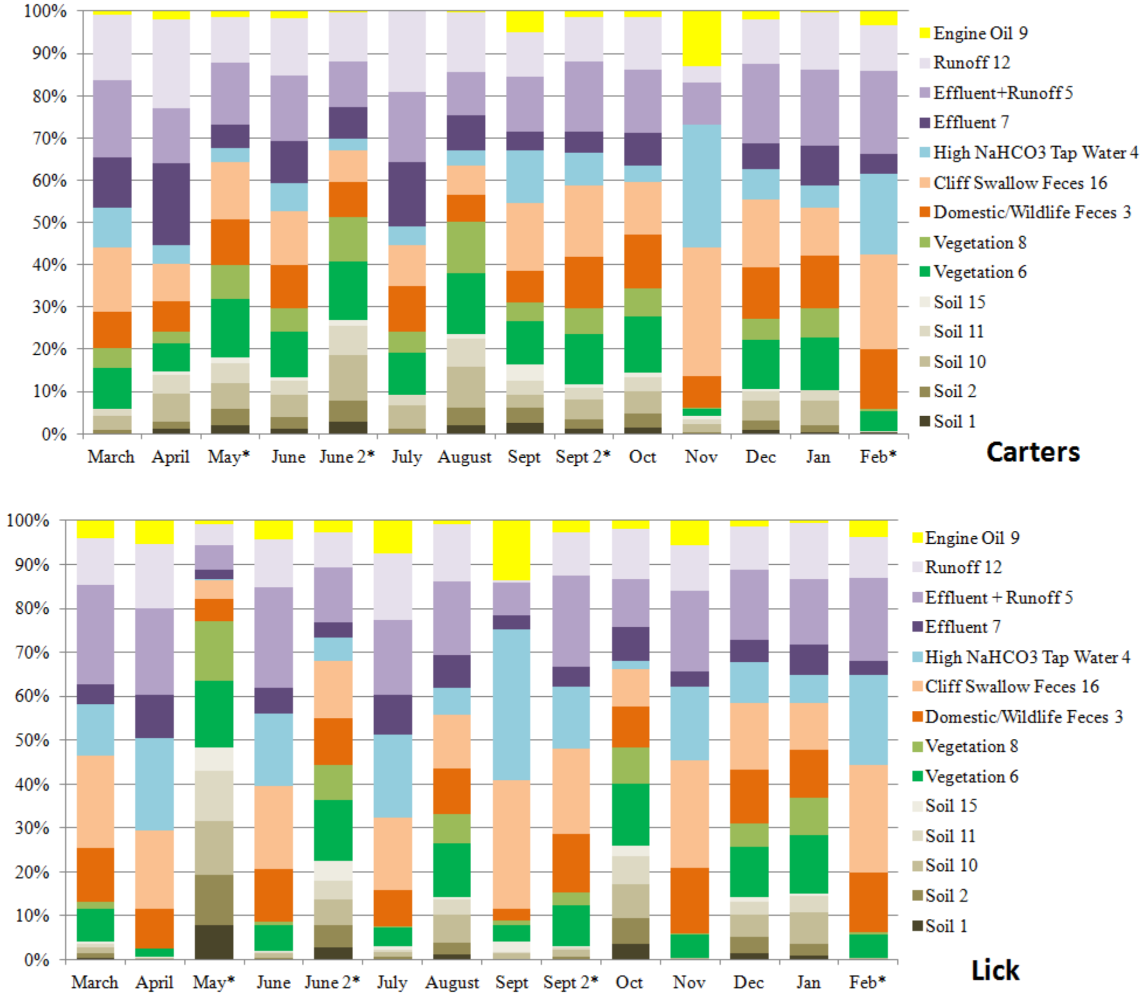

Figure 16. Relative contribution of DOM source material on each sampling date based on stream spectra at WWTP sites. Asterisks indicate rain event.

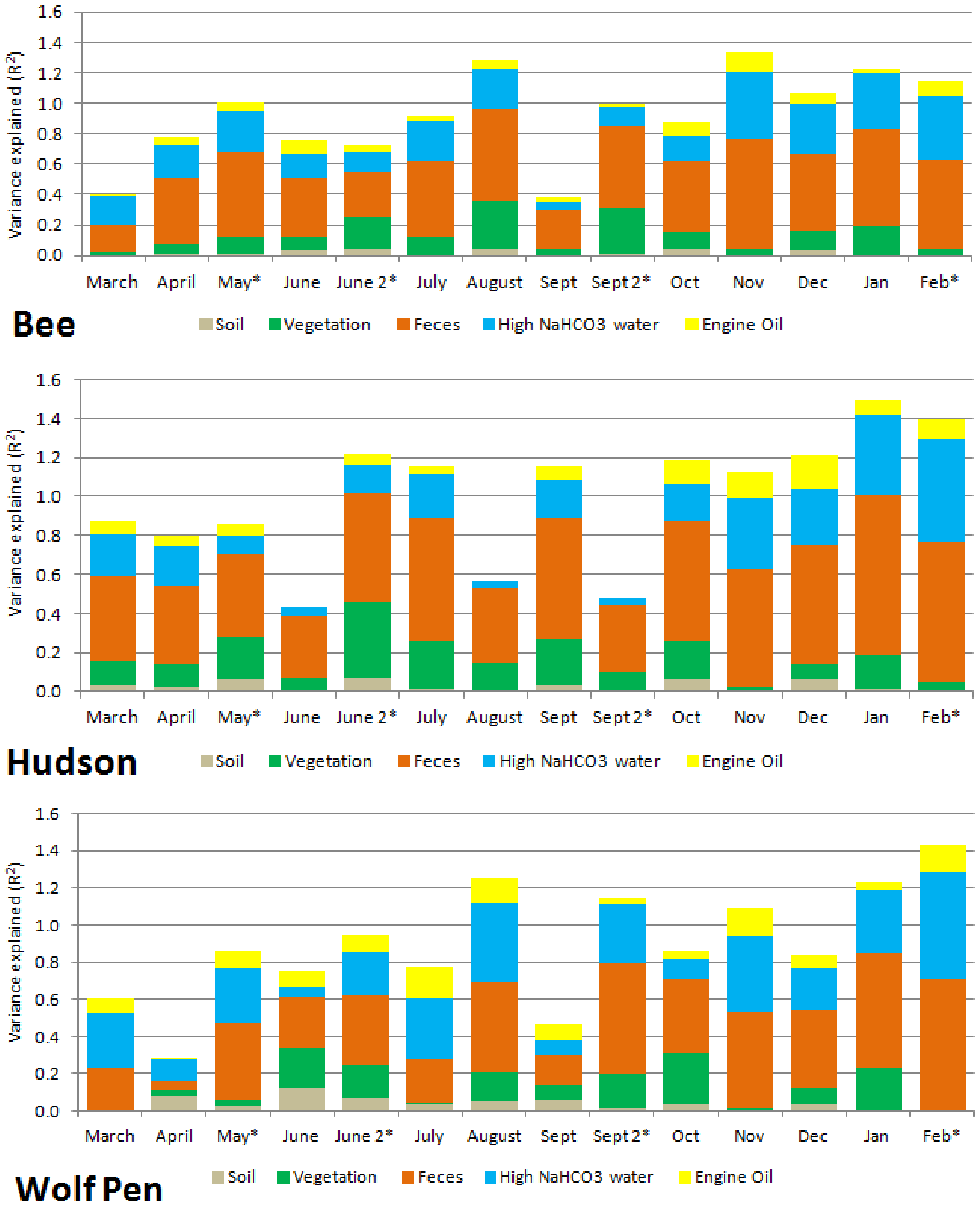

Figure 17. Variance explained (R^2) in urban streams using DOM sources in the WSSL. Askerisks indicate rain event.

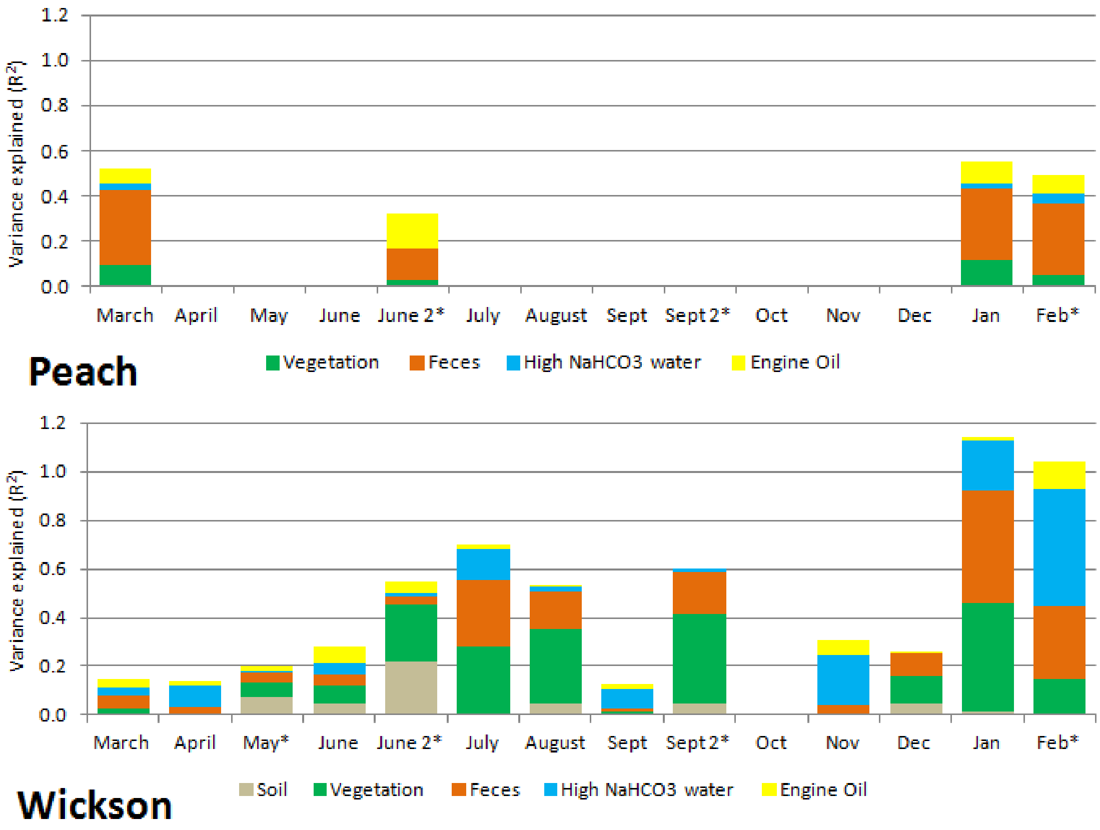

Figure 18. Variance explained (R^2) in rural streams using DOM sources in the WSSL. Askerisks indicate rain event. Peach Creek was dry during 10 of the sampling dates. Wickson Creek was dry during one sampling date. Note different scale on y-axis compared to Figures 17 and 19.

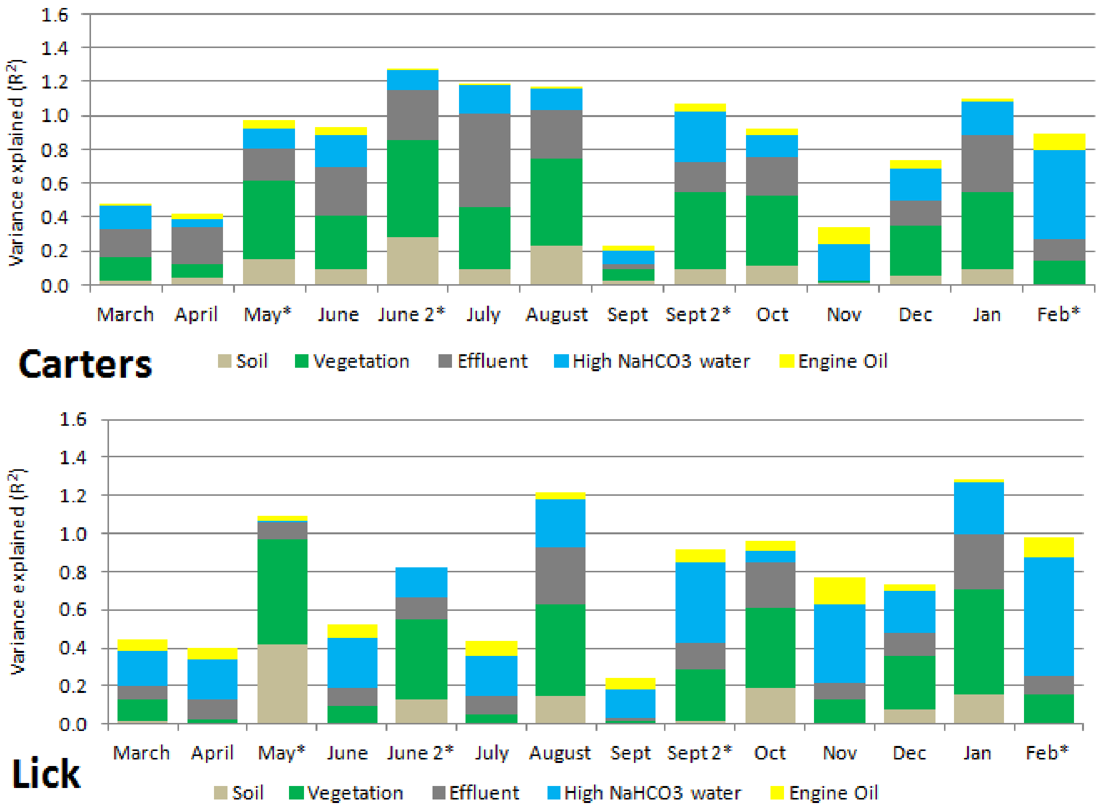

Figure 19. Variance explained (R^2) at WWTP sites using DOM sources in the WSSL. Askerisks indicate rain event.

nest and the bucket was exposed to irrigation water throughout the summer. Municipal tap water high in sodium and bicarbonate is supplied to the entire region, with slightly decreased concentrations in municipal sources in Wickson and Peach Creek watersheds. Municipal tap water is used extensively for irrigation in commercial and residential areas, although its spectral signature is not highly linked to effluent, as suggested by a low correlation. High $NaHCO_3$ water is moderately correlated to group 5 (both runoff and effluent), which may be reflective of irrigation runoff. In urban watersheds, between 5 and 58% (Wolf Pen Creek), 4 and 44% (Bee Creek), and 4 and 53% (Hudson Creek) of the variance in stream spectra was explained by $NaHCO_3$ water. In rural watersheds, high $NaHCO_3$ water explained between 0 and 48% at Wickson Creek and between 0 and 4% at Peach Creek of the variance in stream spectra. It was unexpected that water high in sodium bicarbonate would explain this much variance in rural streams as there is decreased commercial and residential irrigation at these sites. However, more data is needed from rural streams, as only one site has a complete data set (Wickson Creek). At WWTP sites, $NaHCO_3$ water explained between 5 and 53% of the variance in stream spectra at Carters Creek and between 1 and 62% of the variance in stream spectra at Lick Creek.

Engine oil was included in each of the WSSL models to understand its role in storm runoff or illicit dumping into storm drains. The contribution from engine oil in urban streams was between 0 and 17% of the variance in stream spectra in Wolf Pen Creek, 2 and 12% in Bee Creek, and 0 and 17% in Hudson Creek. At the rural sites, between 0 and 12% of the variance in stream spectra was explained by engine oil in Wickson Creek and between 6 and 16% in Peach Creek. In the watersheds with a WWTP, engine oil explained between 0 and 9% of the variance in stream spectra in Carters Creek and between 2 and 14% in Lick Creek.

Isotope analysis

The values for $\delta^{13}C$ ranged from -23.5±0.7‰ at Wolf Pen Creek to -26.8±0.5‰ at Wickson Creek. $\delta^{13}C$ was significantly less at Wickson Creek compared to all other sites except Peach Creek ($p < 0.001$, Figure 20, Table 9). Percent organic carbon ranged from 1.6±2.1% at Carters Creek to 5.8±0.1% at Peach Creek. There were no significant differences for percent organic carbon by site ($p = 0.08$). $\delta^{13}C$ was significantly less at rural sites compared to urban and WWTP ($p < 0.001$, Figure 21). Percent organic carbon was not significantly different between land uses ($p = 0.06$).

Percent organic carbon was significantly higher during the June 2 rain event compared to all other collection dates except January ($p = 0.01$, Figure 22). There were no significant differences for $\delta^{13}C$ based on sampling date.

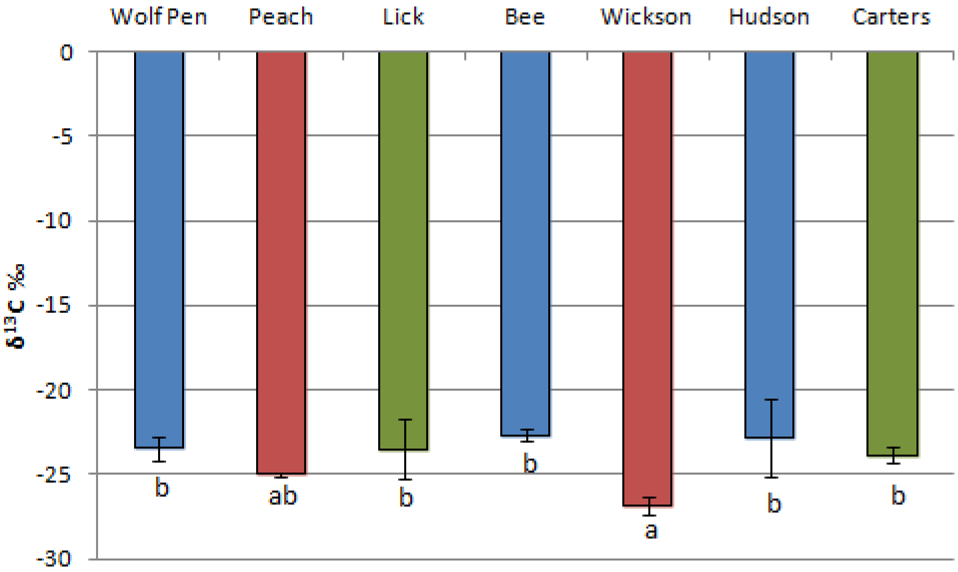

Figure 20. Mean $\delta^{13}C$ ‰ values for streams based on five sampling events. N=5 for all sites except Peach Creek, where N=2. Error bars are standard deviation. Letters indicate significant difference.

Table 9. Summary of $\delta^{13}C$ ‰ and percent organic carbon values for streams. Letters indicate significant differences.

Site	N	$\delta^{13}C$	%OC
Wolf Pen	5	-23.46^{b}	1.97^{a}
Peach	2	-25.00^{b}	5.83^{a}
Lick	5	-23.50^{b}	1.74^{a}
Bee	5	-22.68^{ab}	3.97^{a}
Wickson	5	-26.84^{a}	3.58^{a}
Hudson	5	-22.82^{b}	4.44^{a}
Carters	5	-23.86^{b}	1.63^{a}

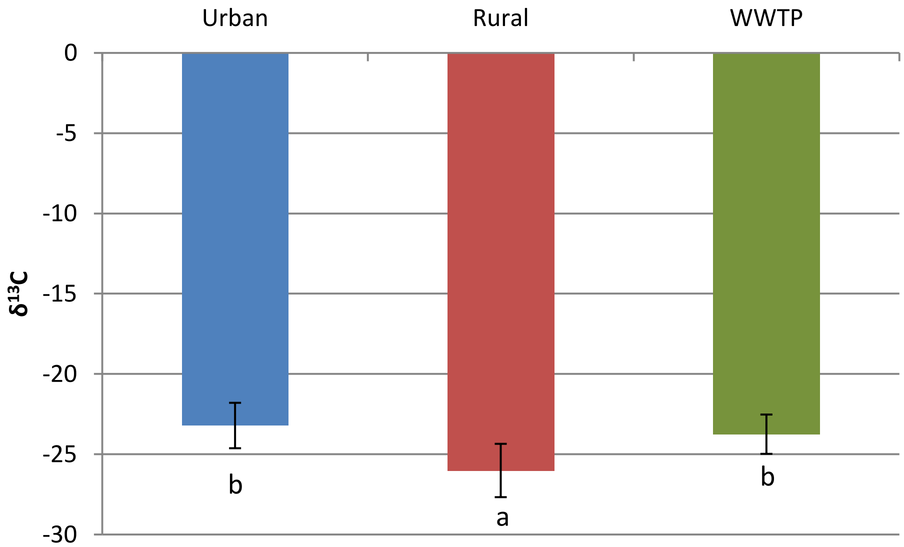

Figure 21. Mean $\delta^{13}C$ ‰ values for streams grouped by land use classification. Error bars are standard deviation. Letters indicate significant difference.

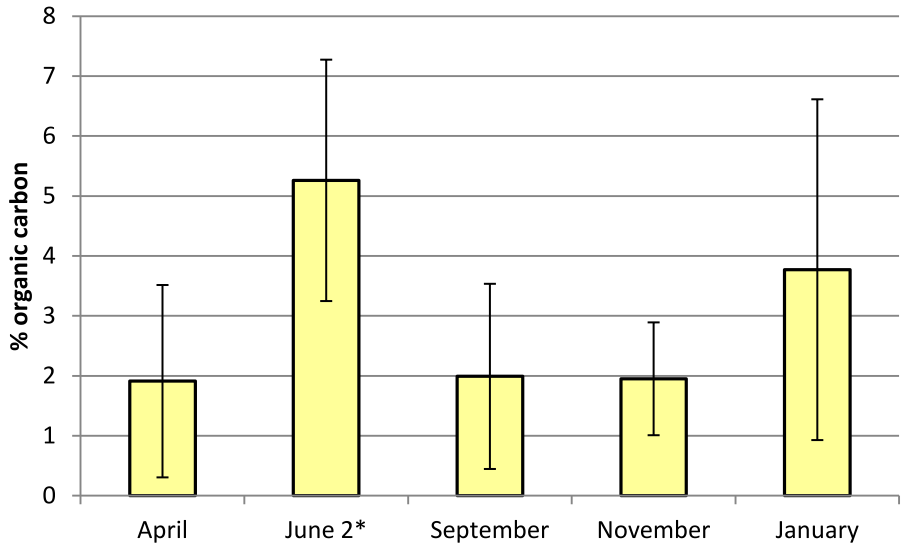

Figure 22. Percent organic carbon in streams grouped by sampling date. Asterisk indicates rain event. Error bars are standard deviation. Letters indicate significant difference.

Links between DR-NIR spectra and isotope analysis

A partial least squares regression (PLSR) was performed using chemometric software (Unscrambler, v. 9.8) in order to explore a possible relationship between DR-NIR spectra and carbon isotope values. Eighty eight percent of the variance in carbon isotope values was explained by stream spectra (Figure 23). A simple validation model was constructed to predict missing carbon isotope values (leave one out cross validation) to generate a table of observed and predicted carbon isotope values. The predicted and observed values were transferred to a scatter plot and a trend line was added to observe the capability of stream water DR-NIR spectra to predict carbon isotope values. There was a strong significant relationship between observed and predicted $\delta^{13}C$ ‰ values (adjusted $R^2 = 0.88$; $p < 0.001$).

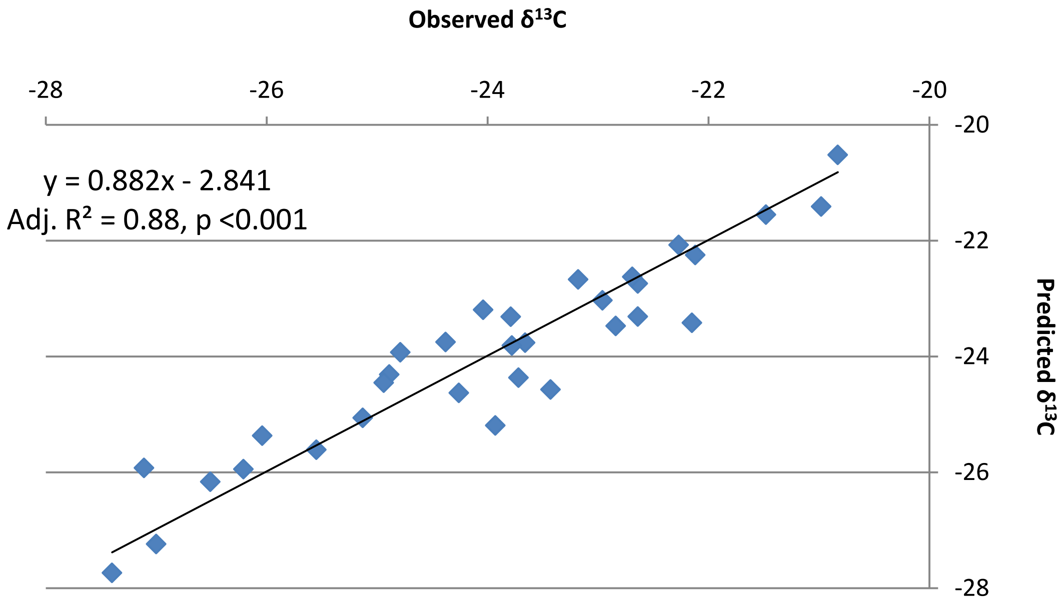

Figure 23. Predicted and observed $\delta^{13}C$ ‰ values. Predicted values are based on DR-NIR stream spectra.

Vegetation and soil extract chemistry

Mean water extractable DOC (WEDOC) in vegetation extracts ranged from 213±89 mg/L in forests to 800±67 mg/L in pasture. Concentrations of WEDOC in forest and range/shrub scrub vegetation extract was significantly lower than from pasture and developed open vegetation (p = 0.004, Figure 24).

Mean WEDOC in soil solutions ranged from 17±10 mg/L for developed low areas to 42±17 mg/L in highly developed regions (Figure 25). Mean water extractable pH ranged from 6.8±0.5 in pasture to 9.3±0.8 in highly developed areas. Mean EC ranged from 19±8 µS/cm in range/shrub scrub to 522±582 µS/cm in developed open areas. There were no significant differences in WEDOC, pH, or EC in soil based on land use.

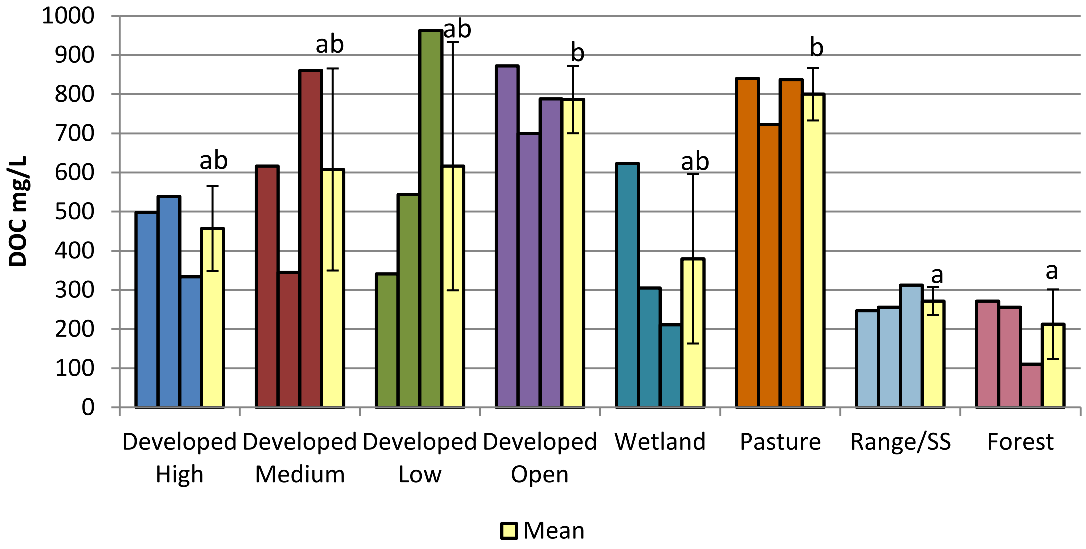

Figure 24. WEDOC in vegetation extracts. Three replicates and the mean value are shown for each land use. Error bars are standard deviation. Letters indicate significant difference.

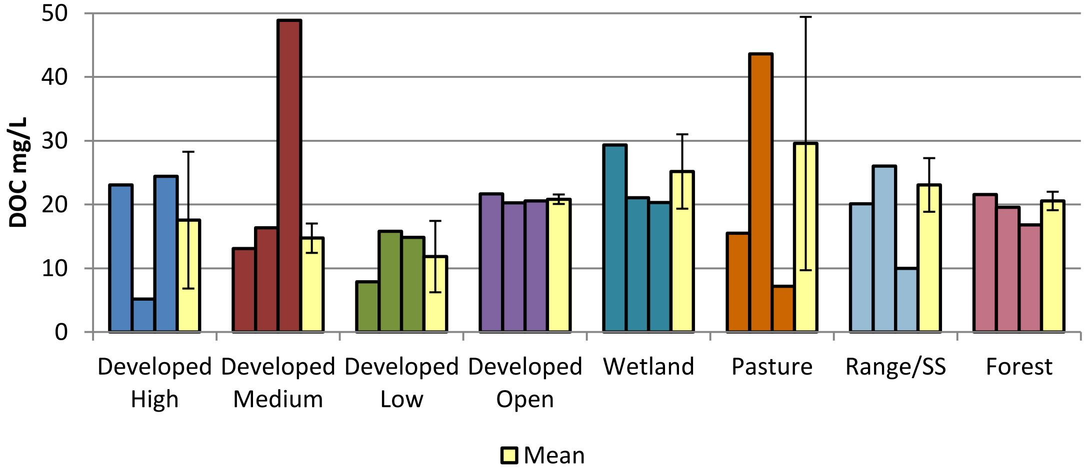

Figure 25. WEDOC in soil extracts. Three replicates and the mean value are shown for each land use. Error bars are standard deviation.

Mean water extractable sodium ranged from 2±0.8 mg/L in pasture to 50±28 mg/L in developed open areas. Sodium was significantly higher in developed open areas compared to all land uses, except for highly developed regions ($p < 0.001$, Figure 26). Water extractable soil calcium was significantly higher in developed open areas from all other land uses ($p < 0.001$, Figure 27) and ranged from 1±0.17 mg/L for range/shrub scrub to 15±7 mg/L in developed open areas. There was no land use effect on water extractable soil potassium and magnesium. SAR ranged from 0.4±0.1 in pasture to 3.9±2.1 in developed open areas and was significantly different between these two land uses ($p = 0.003$, Figure 28).

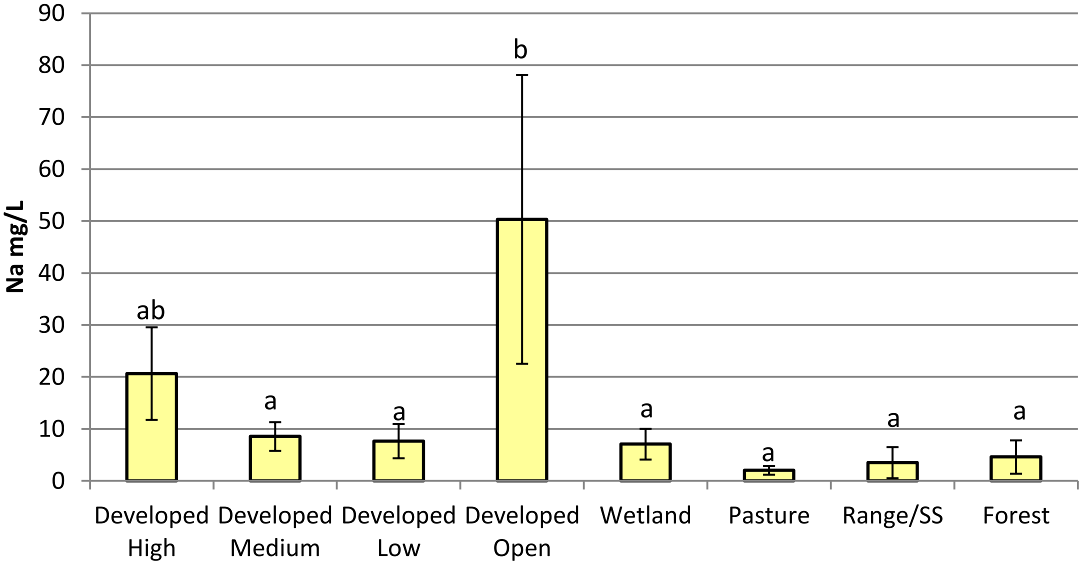

Figure 26. Mean water extractable soil sodium. Error bars are standard deviation. Letters indicate significant difference.

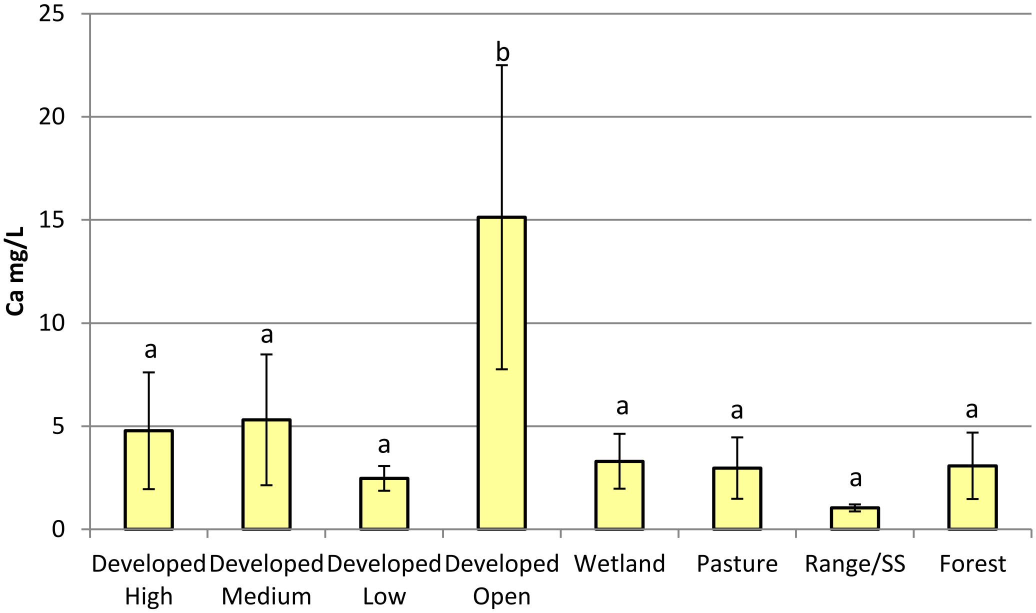

Figure 27. Mean water extractable soil calcium. Error bars are standard deviation. Letters indicate significant difference.

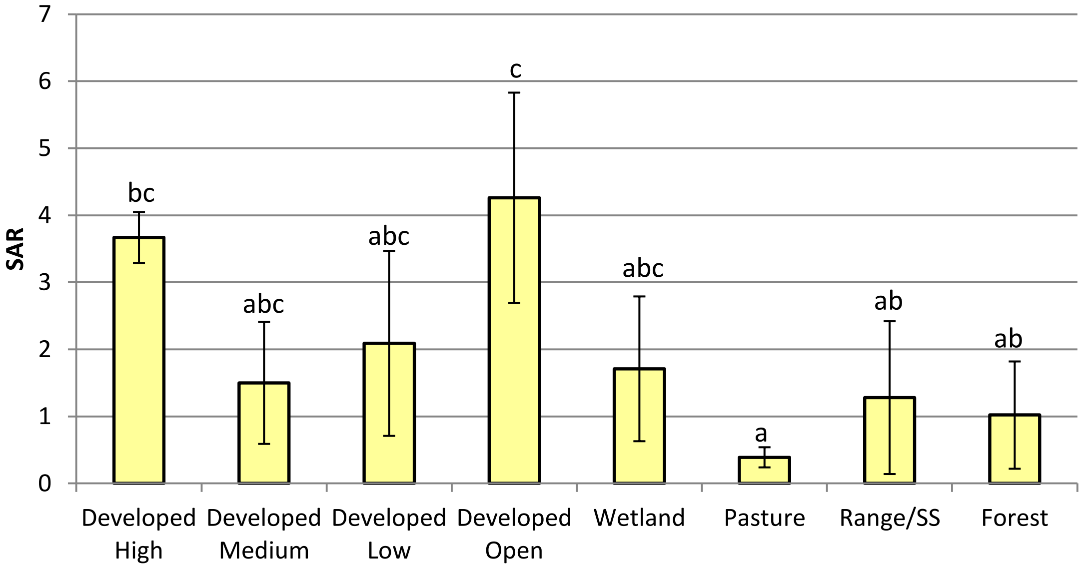

Figure 28. Sodium adsorption ratio (SAR) in soil extracts. Error bars are standard deviation. Letters indicate significant difference.

In most cases, soil chemistry was influenced by land use. Soil pH, as measured in a 1:10 soil:water extract, was highest at developed open and highly developed sites (pH 8.9 and 9.3), illustrating the effect of irrigation with tap water high in sodium. A positive correlation was found between pH and water extractable soil sodium ($r = 0.43$, $p = 0.04$) as well as pH and land use ($r = 0.46$, $p = 0.03$). While there was no significant different between land uses, urban sites had a pH of 8.4 compared to a pH of 7.3 in non urban sites. Soil EC was also highest at developed open and highly developed sites (522 and 105 µS/cm). No significant difference was recorded among land uses, but urban sites had a higher conductivity than non urban sites (188 and 29 µS/cm respectively). Urban sites with medium and low intensity of development had much lower conductivities (84 and 43 µS/cm), which were more in line with non urban regions. A positive correlation was found between EC and water extractable soil sodium ($r = 0.86$, $p < 0.001$). Lower conductivity, along with lower pHs at these same two sites (pH 7.7 and 7.8), suggests that less intensive irrigation, or even no irrigation at all, may have taken place. Soil pH was significantly higher at urban sites ($p = 0.01$) while EC was not ($p = 0.10$).

The highest concentrations of water extractable sodium were recorded at highly developed and open urban areas. Open developed areas, typically recreational parks, had a significantly higher sodium concentration due to increased inputs of sodium through irrigation. Water extractable soil sodium was significantly higher at urban sites ($p= 0.01$), with an average of 22 mg/L in urban sites, compared to 4 mg/L at non urban areas. Water extractable calcium was significantly higher in urban open areas compared to all other land uses. Water extractable sodium adsorption ratio was highest at urban open areas and highly developed sites due to increased concentrations of the sodium ion at these locations. Water extractable soil SAR was significantly higher in urban regions compared to non urban regions (2.8 and 1.1, $p = 0.002$). Soil SAR was correlated to most soil parameters, indicating the importance of sodium relative to calcium and magnesium.

Water extractable DOC (WEDOC) in soil was highest at highly developed and open urban areas, the two locations subjected to the greatest intensity of irrigation with high sodium tap water. Positive correlations were also found between WEDOC and water extractable soil sodium ($r = 0.50$, $p = 0.01$), WEDOC and pH ($r = 0.59$, $p = 0.002$), and WEDOC and SAR ($r = 0.57$, $p = 0.03$). While there were no significant differences in WEDOC among land uses, there was variation within replicates. For example, one of the developed medium sites has much higher WEDOC values than the other two replicates (48 mg/L vs. 16 and 13 mg/L).

Fates of dissolved organic carbon in rural and urban watersheds

Stream chemistry

Dissolved organic carbon in streams can be considered to be a fate of terrestrial, or allochthonous, DOC. Mean annual DOC in stream water ranged from 11±3 mg/L in Carters Creek to 31±12 mg/L in Hudson Creek. DOC concentrations in Lick and Carters Creeks were significantly lower than in Bee Creek and Hudson Creek ($p < 0.001$, Figure 29). Urban streams had significantly higher DOC than WWTP streams ($p < 0.001$, Figure 30).

Mean annual pH varied from 7.8±0.2 in Peach Creek and 7.8±0.4 in Wickson Creek to 8.5±0.7 at Wolf Pen Creek and was significantly different between these two rural sites and one urban site ($p = 0.005$, Figure 31). pH was not significant based on land use ($p = 0.06$), but was significantly higher in the summer and fall compared to spring ($p < 0.001$, Figure 32). Mean annual EC ranged from 388±185 µS/cm at Peach Creek to 1262±632 µS/cm at Wolf Pen Creek and was significantly different between these two sites ($p < 0.001$, Figure 33). Rural streams had significantly lower EC compared to urban and WWTP streams ($p < 0.001$, Figure 34). There were no significant seasonal effects for DOC or EC, but some sites had increases of DOC in the summer and fall (Figure 35).

Simple stream chemistry measurements, such as pH and conductivity, provide valuable context for understanding DOC in streams. Mean annual pH was significantly lower at rural sites, which is likely due little to no irrigation with high sodium tap water in these watersheds. The higher pH at rural watersheds recorded in summer and fall can be attributed to high pH baseflow. Mean annual EC was significantly lower at Peach Creek compared to Wolf Pen Creek. Again, exposure to high sodium irrigation water is the likely culprit as Wolf Pen is a 100% urbanized watershed with a high percentage of irrigated recreational parks compared to rural land uses in the Peach Creek watershed. Additionally, EC was significantly lower at rural sites compared to both urban and WWTP streams. Irrigation exposure can explain the increased urban EC, while salts associated with the water treatment process likely contribute to an increased EC at WWTP sites. While season did not significantly affect EC ($p = 0.06$), conductivity was higher in summer and fall (1039 µs/cm average) compared to winter and spring samples (780 µs/cm average), which is also attributable to increased irrigation during the summer and fall seasons. Both pH and EC were significantly lower during rain events due to the dilution of salts ($p < 0.001$). A positive correlation was found between pH and EC in streams ($r = 0.61$, $p < 0.001$).

Streams with WWTPs typically have higher DOC concentrations compared to other streams (Westerhoff and Anning 2000). In my study, mean annual DOC was lower in streams with WWTP which may be due to increased processing of carbon by microbes used in the treatment process. The higher DOC seen in urban streams may be due to sodium inputs from irrigation with high sodium tap water (Aitkenhead-Peterson et al. 2009). Westerhoff and Anning (2000) showed that urban infrastructure, such as reservoirs and impoundments, can support processes that can cause an increase in DOC in surface waters through algal growth and atmospheric deposition. The urban sites in my study typically had very low, slow moving flows, which may be functioning similarly to ponded water. This may help to explain the significantly higher DOC seen in urban streams. Variance in surface water DOC was lowest at WWTP sites, likely due to consistent effluent inputs. Previously, stream DOC concentrations have been linked to urban open area (Aitkenhead-Peterson et al. 2009). The DOC concentrations in my study did not correlate to any land use. There was not a significant increase in DOC during the fall as is often typical in northern forested regions due to heavy inputs of organic matter from leaf litter (Hongve 1999). Surface water DOC increased slightly in summer and fall (average of 18.8 mg/L among all sites compared to 16.4 mg/L in winter and spring), but this trend was not significant.

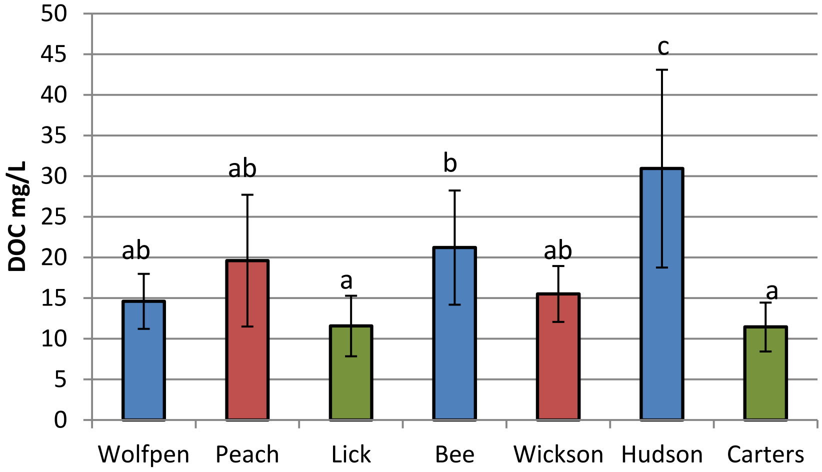

Figure 29. Mean annual DOC concentrations in streams (mg/L). Error bars are standard deviation. Letters indicate significant difference. Blue columns are classified as urban, red as rural, and green as WWTP.

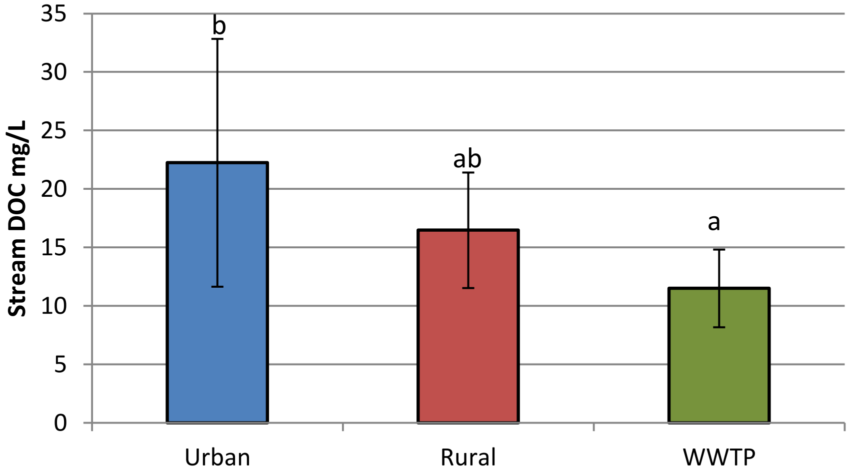

Figure 30. Mean annual DOC concentrations in streams (mg/L) grouped by land use classification. Error bars are standard deviation. Letters indicate significant difference.

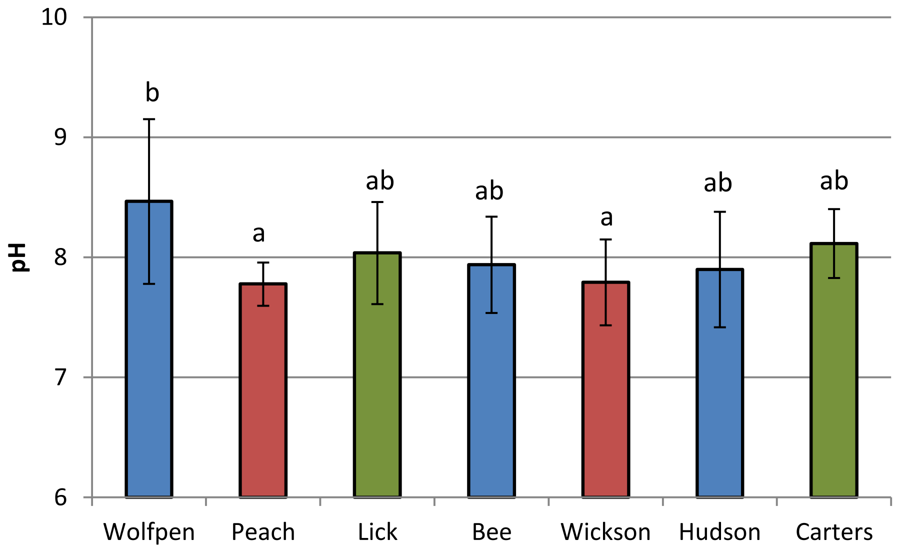

Figure 31. Mean annual pH in streams. Error bars are standard deviation. Letters indicate significant difference. Blue columns are classified as urban, red as rural, and green as WWTP.

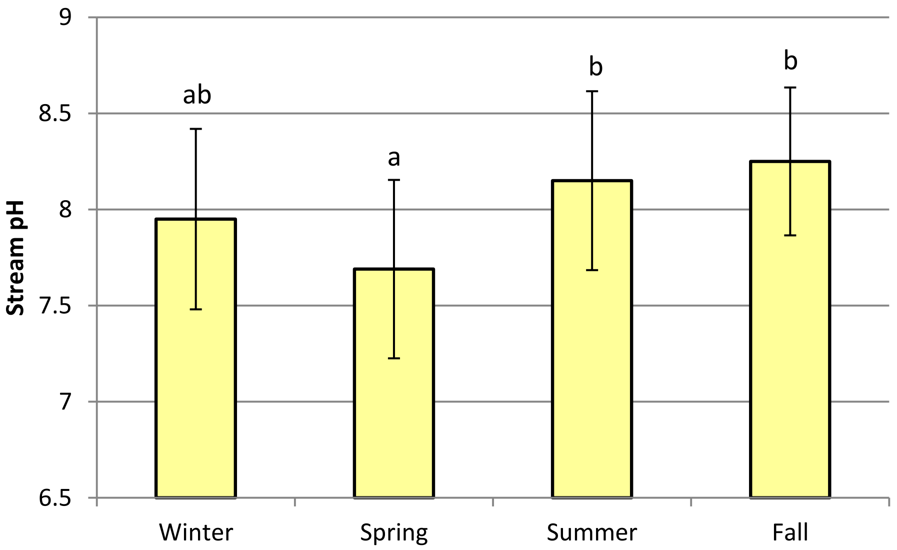

Figure 32. Mean annual stream pH grouped by season. Error bars are standard deviation. Letters indicate significant difference.

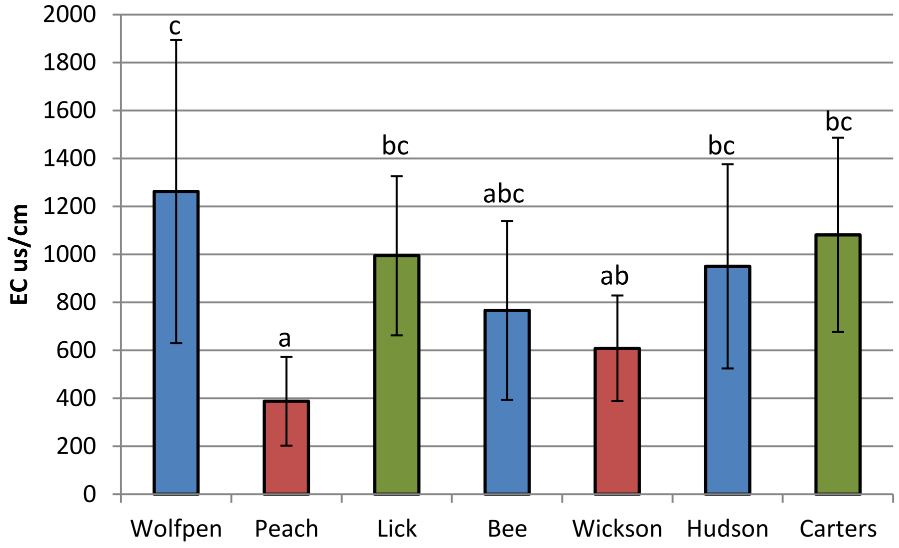

Figure 33. Mean annual EC (µS/cm) in streams. Error bars are standard deviation. Letters indicate significant difference. Blue columns are classified as urban, red as rural, and green as WWTP.

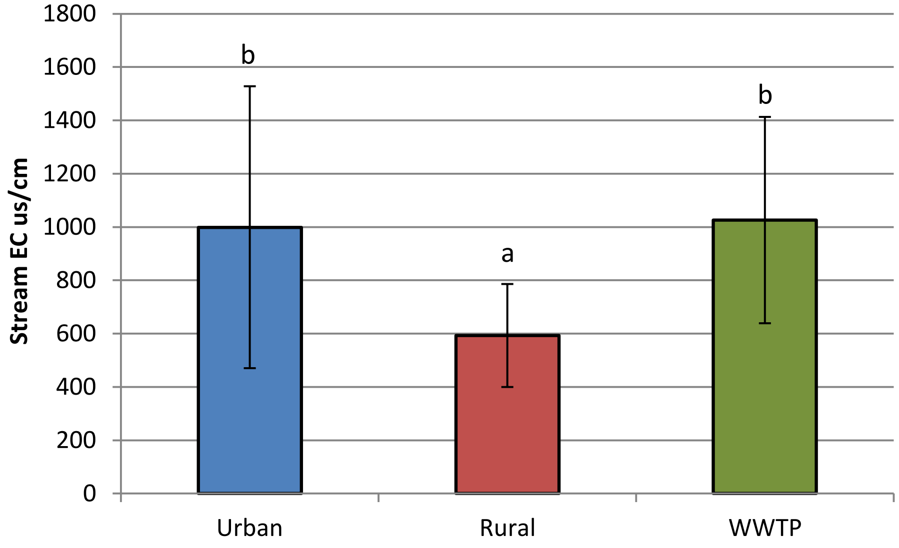

Figure 34. Mean annual EC (µS/cm) in streams grouped by land use classification. Error bars are standard deviation. Letters indicate significant difference.

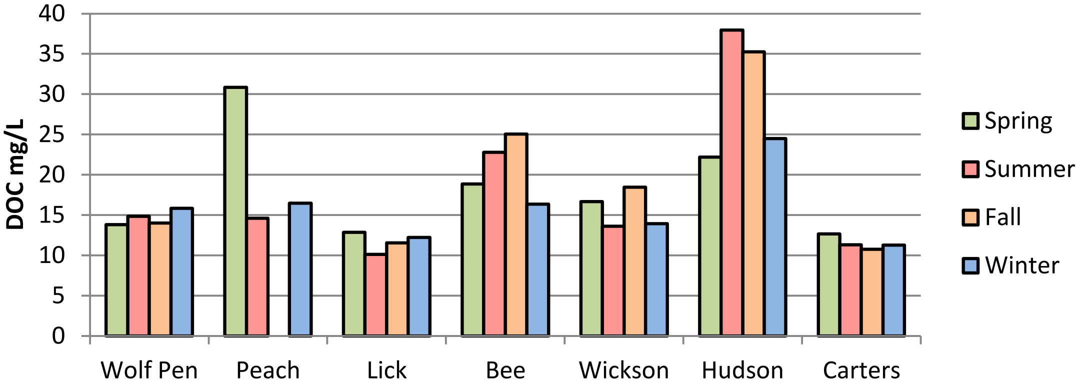

Figure 35. DOC (mg/L) in streams grouped by season. Spring was defined as March, April, and May, and rest of the seasons are the follow three month periods thereafter. Peach Creek was dry throughout the fall season.

Biodegradability

Analysis of the biodegradability of a glucose solution used as a check found that inoculant microbes successfully used the DOC available in solution for all incubations conducted during this study (vegetation, soil, and stream, Figure 36).

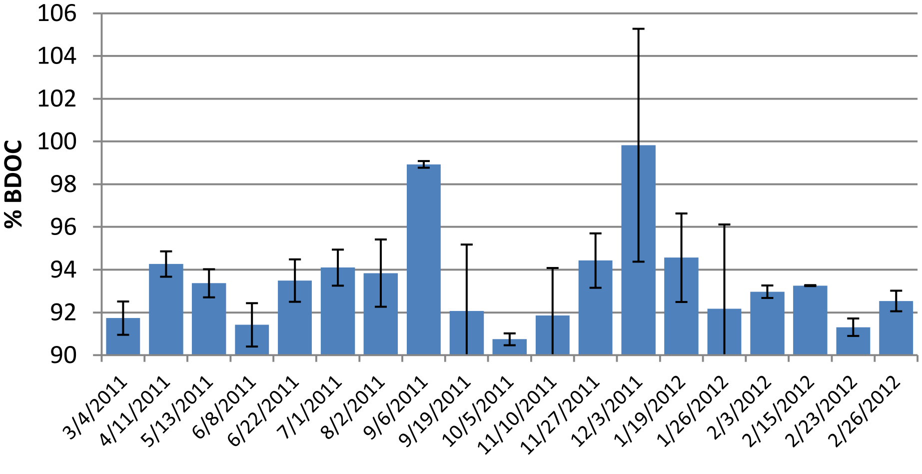

Figure 36. Biodegradability of glucose solution. Biodegradability over 90% indicated that the inoculants microbe successfully utilized the DOC available in solution. Error bars are standard deviation.

Vegetation biodegradability

Mean BDOC ranged from 34±3% for forests to 75±4% for developed low areas. Significant differences for %BDOC in vegetation were recorded between forest, wetland, and developed low regions ($p < 0.001$, Figure 37).

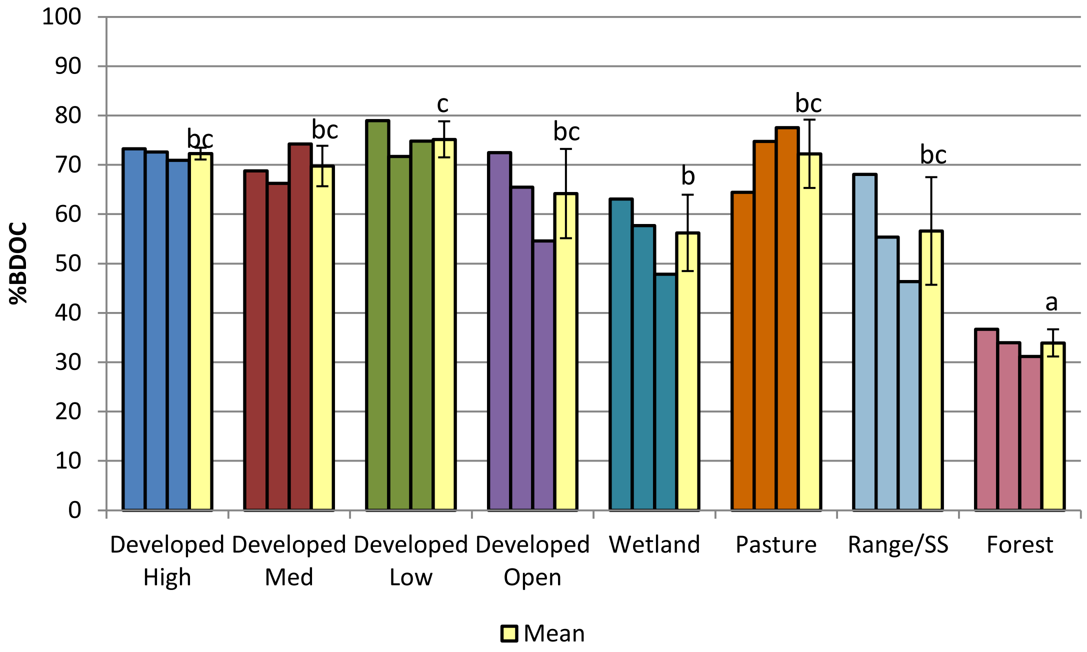

Figure 37. Percent biodegradable dissolved organic carbon (%BDOC) in vegetation extracts. Three replicates and the mean value are shown for each land use. Error bars are standard deviation. Letters indicate significant difference.

Soil biodegradability

Values for soil BDOC in the study watersheds ranged from 47±1% in urban medium developed regions (composed of mixed warm and cool season grasses and associated weeds) to 19±3% in soil under wetlands (Figure 38). The increased BDOC in soils beneath land uses dominated by grass, relative to soils beneath woody species, likely reflects a greater proportion of refractory compounds of DOC in forest vegetation.

The null hypothesis that there would be no significant differences in soil BDOC based on land use ($H0_{2b}$) was not rejected ($p = 0.80$, $\alpha = 0.01$).

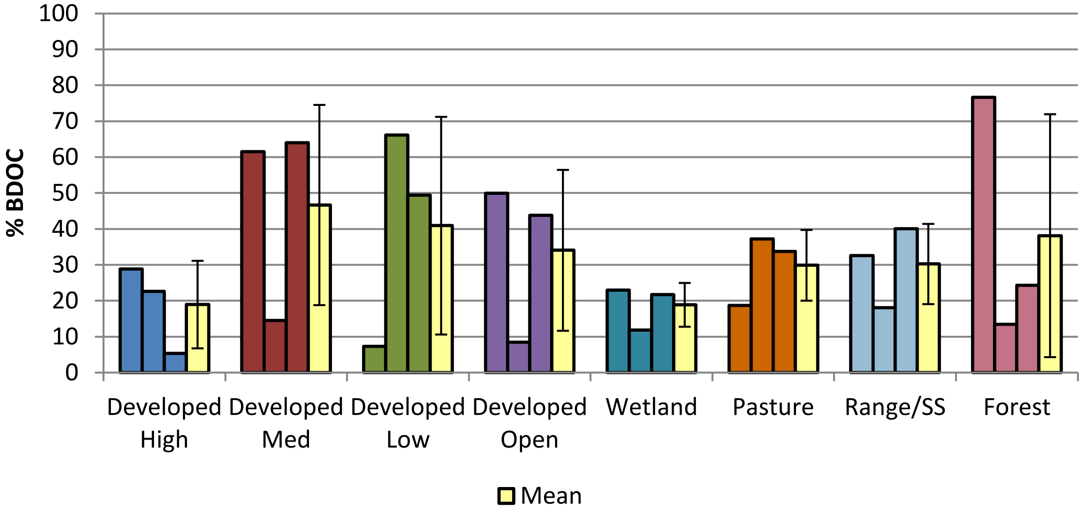

Figure 38. Percent biodegradable dissolved organic carbon in soil extracts. Three replicates and the mean value are shown for each land use. Error bars are standard deviation.

Stream biodegradability

Mean annual BDOC ranged from 5±5% in Wolf Pen Creek to 10±7% in Wickson Creek. There were no significant differences in %BDOC among streams (Figure 39). Percent BDOC over the sampling period is shown by site in Figures 40-42.

The hypothesis that BDOC would be higher in watersheds with less urban land use and in watersheds with WWTP due to a younger, more labile, source of DOC (H2) was rejected as there were no significant differences in BDOC among streams ($p = 0.06$, $\alpha = 0.01$). However, BDOC was highest in rural watersheds (9.7%), followed by WWTP watersheds (6.1%), and lastly urban watersheds (5.2%). It appears that this trend in the data may support the hypothesis, which was based on the influence of high sodium irrigation water removing refractory compounds adsorped to soil.

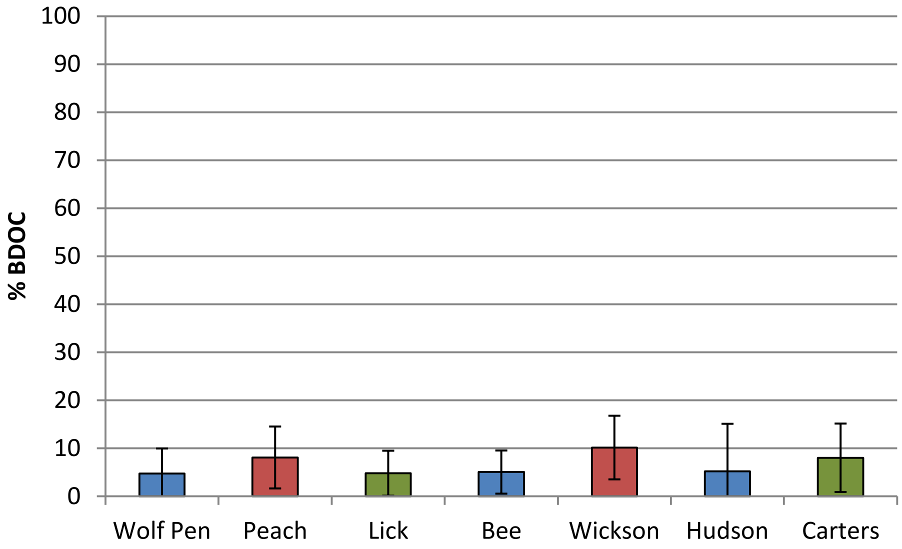

Figure 39. Mean annual %BDOC concentrations in streams. Error bars are standard deviation. Blue streams are classified as urban, red as rural, and green as WWTP. Axis is set to 100% in order to allow easy comparison to soil and vegetation BDOC figures.

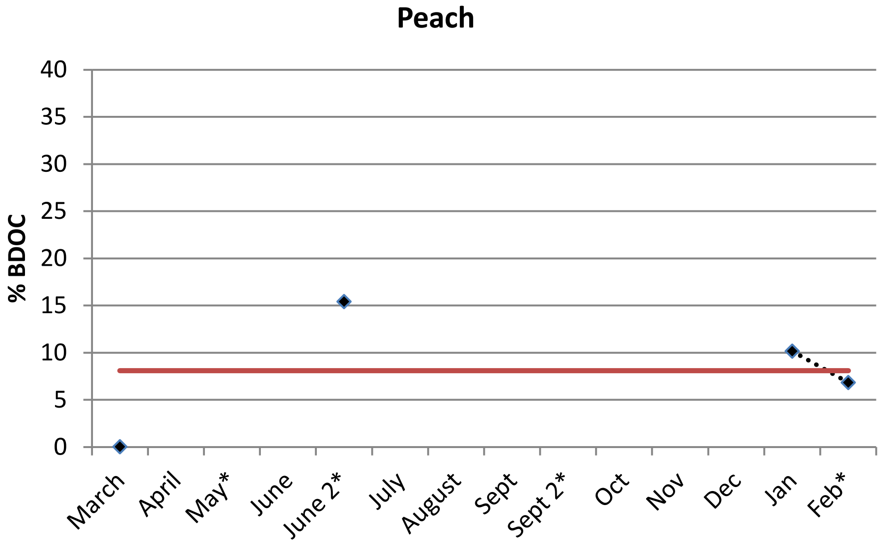

Figure 40. Biodegradability in Peach Creek. Samples were collected four out of fourteen sampling dates as stream was dry for most of the sample period. Red line is mean annual average %BDOC. Asterisks indicate rain event.

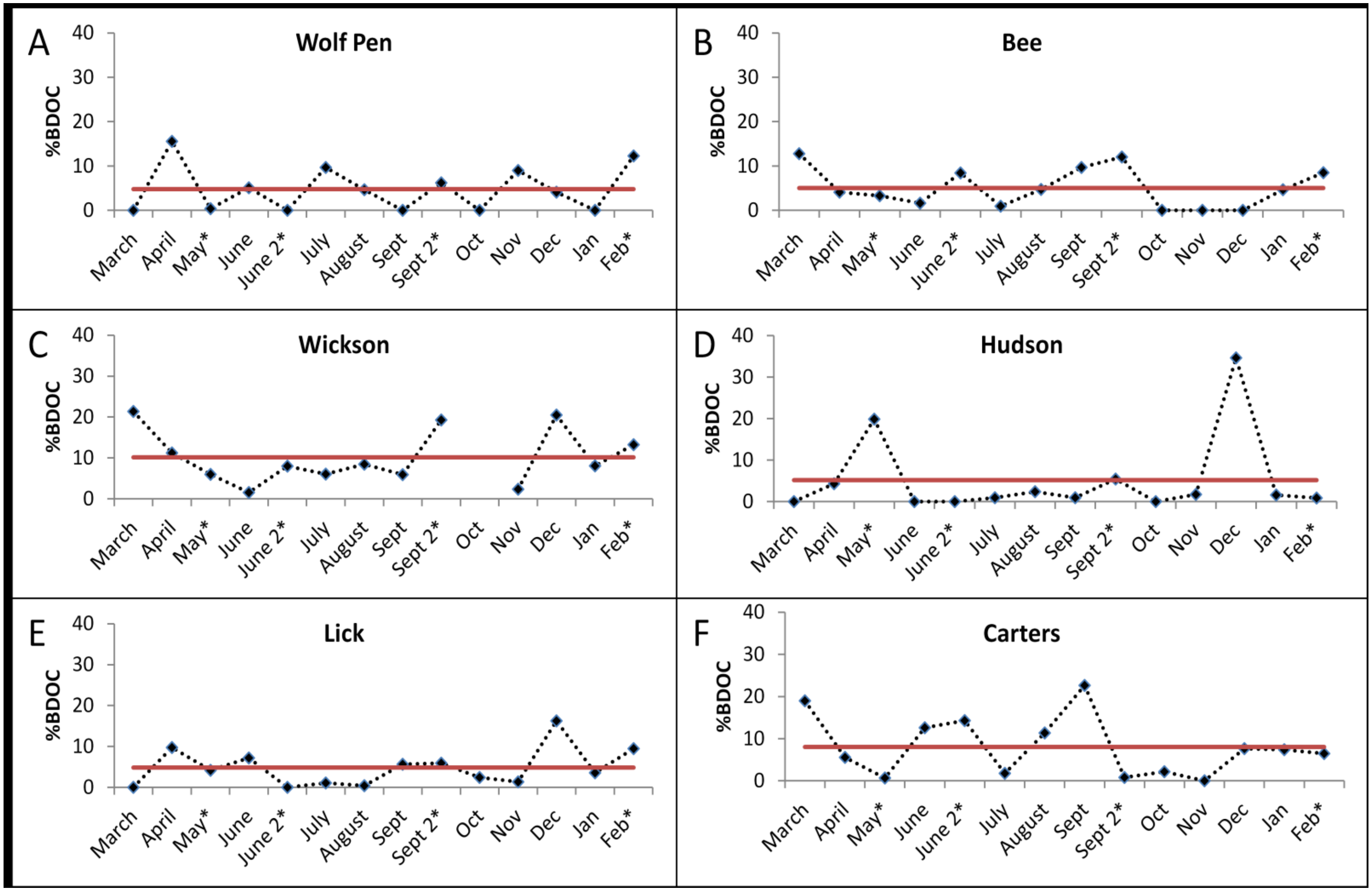

Figure 41. Biodegradability in streams shown by month. Red line is mean annual average %BDOC. Asterisks indicate rain event. Wickson Creek was dry in October and was not sampled.

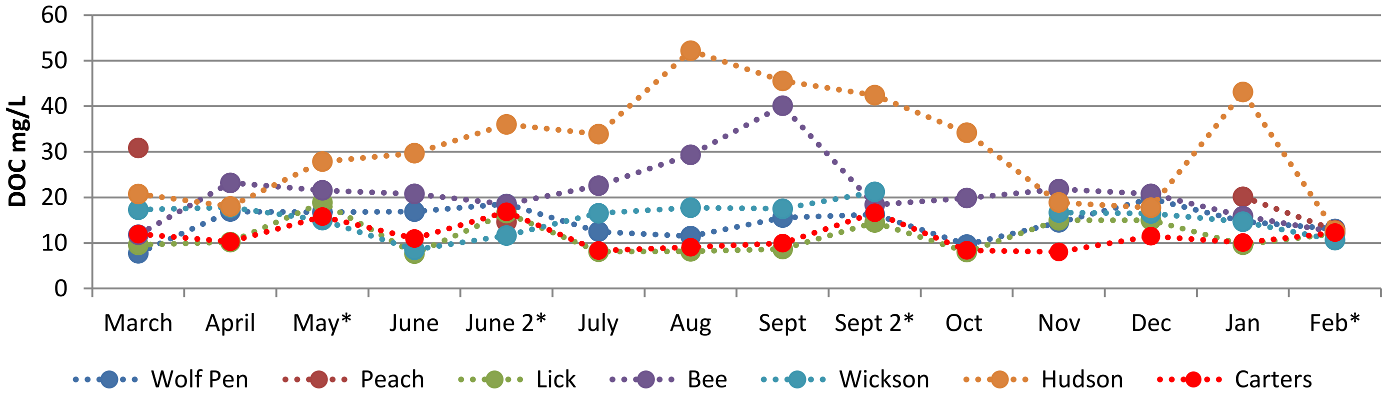

Figure 42. Biodegradability in all streams shown over the sampling period. Asterisks indicate rain event.

Soil adsorption

Isotherms for urban and non urban sites are shown in Figures 43 and 44. The adsorption coefficient, m, ranged from 0.13±0.13 in pasture to 0.33±0.04 in wetland soils (Figure 45). Higher values for the adsorption coefficient, m, are indicative of a better ability to adsorp carbon. The adsorption coefficient for pasture was significantly lower than for developed high and wetland soils ($p = 0.006$). Values for the release term, b, ranged from 85±41 mg/kg in range/shrub scrub soils to 412±152 mg/kg in highly developed areas (Figure 46). Reactive soils pools (RSP), a measure of the amount of DOC that is likely to be leached from soil, varied from 108±53 mg/kg in range/shrub scrub to 647±660 mg/kg for developed open areas (Figure 47). Equilibrium values for DOC ranged from 15±2 mg/L in range/shrub scrub soils compared to 49±20 in highly developed areas (Figure 48). Percent soil adsorption at the highest input concentration ranged from 4±3% in developed open areas to 12±3% in medium development regions (Figure 49). Soil SAR was correlated to most soil parameters (Table 10). Significant positive correlations were found between pH and several soil parameters (Table 11). There were no significant differences for b, RSP, equilibrium DOC, or percent adsorption based on land use.

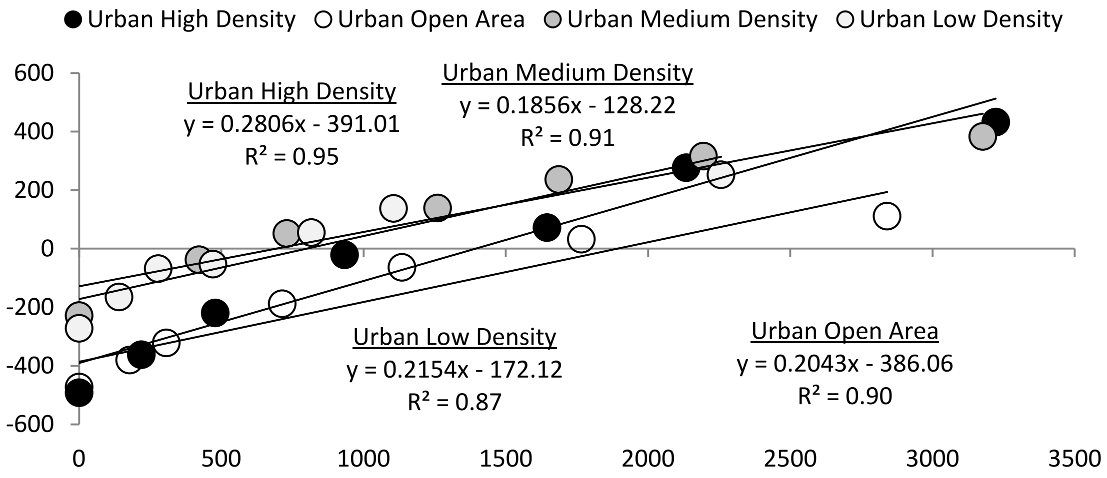

Figure 43. Initial mass isotherms for urban soil sites.

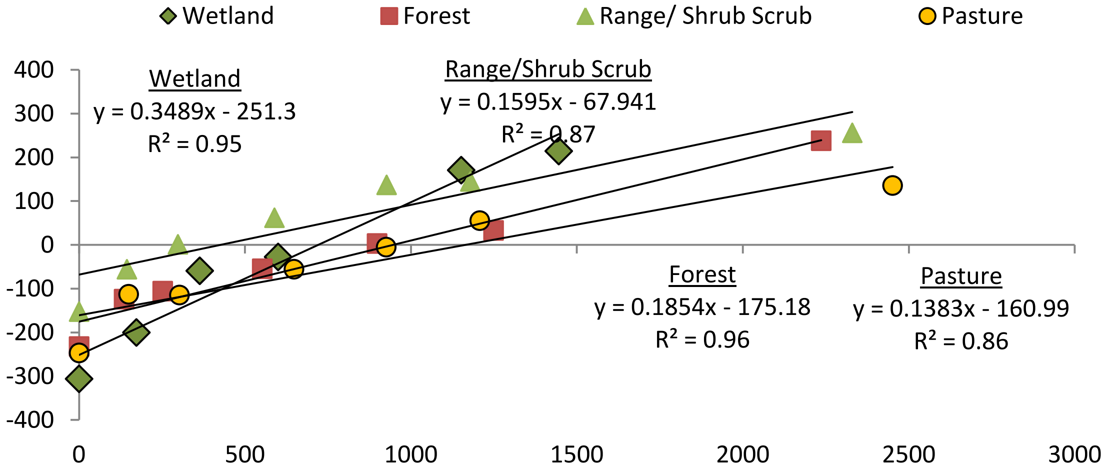

Figure 44. Initial mass isotherms for non urban soil sites.

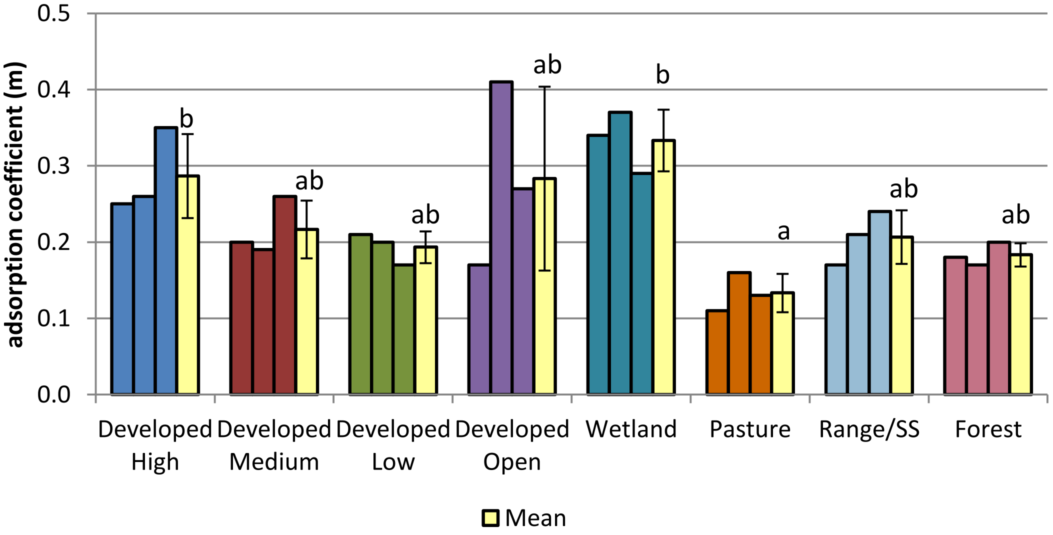

Figure 45. Adsorption coefficient (m) for soils in land use classes. Three replicates and the mean value are shown for each land use. Error bars are standard deviation. Letters indicate significant difference.

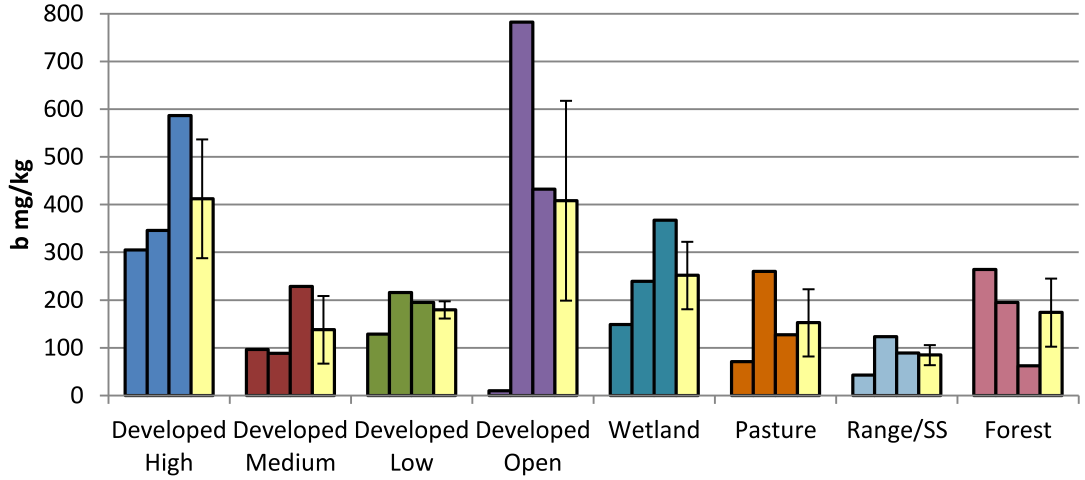

Figure 46. Release term (b) for soils in land use classes. Three replicates and the mean value are shown for each land use. Error bars are standard deviation.

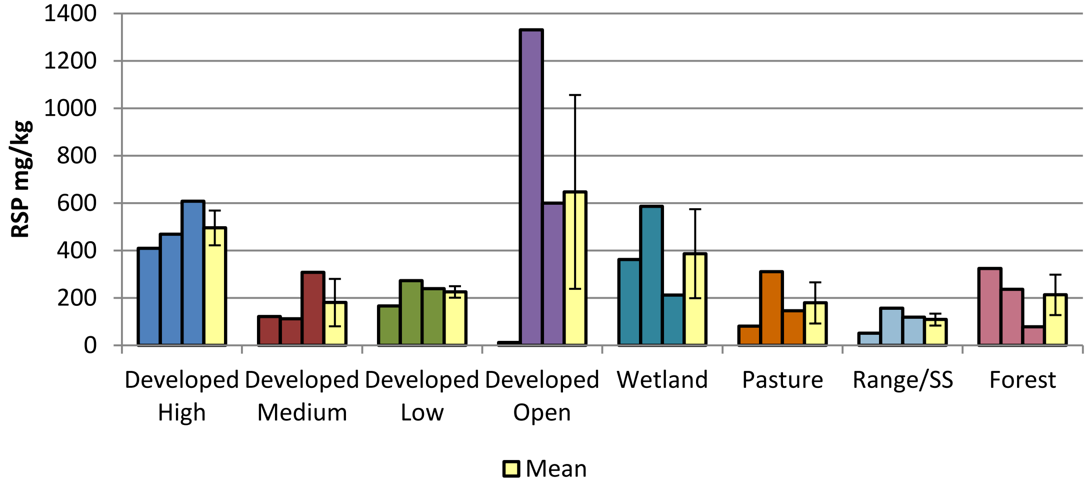

Figure 47. Reactive soil pool (RSP) for soils in land use classes. Three replicates and the mean value are shown for each land use. Error bars are standard deviation.

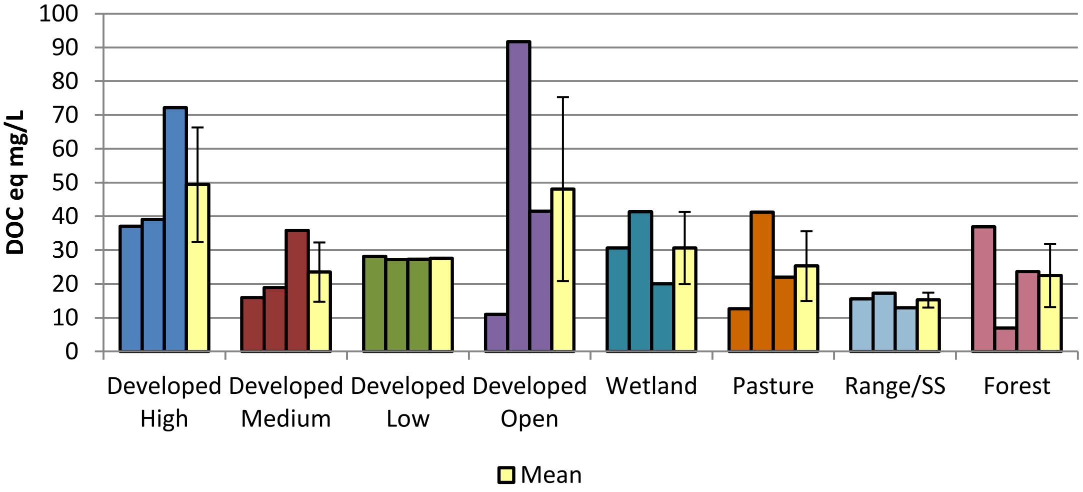

Figure 48. Equilibrium DOC (mg/L) for soils in land use classes. Three replicates and the mean value are shown for each land use. Error bars are standard deviation.

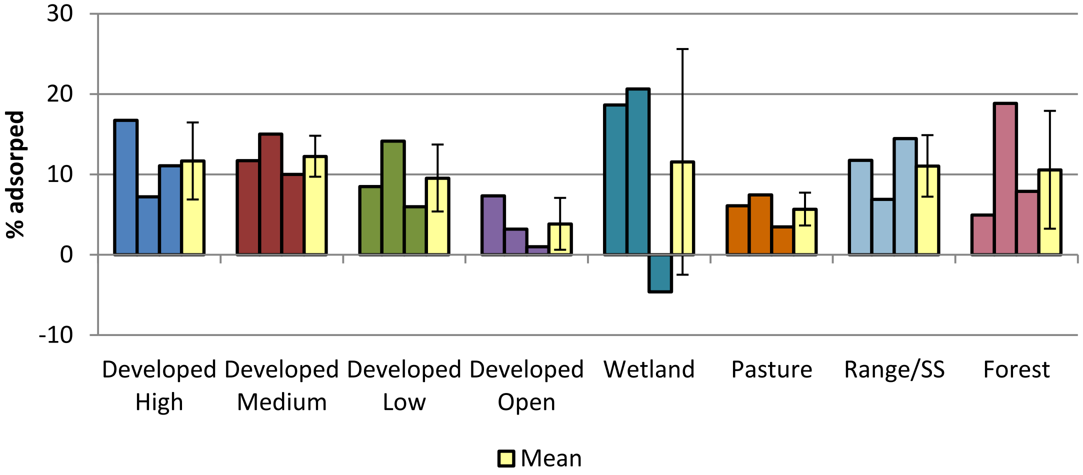

Figure 49. Percent of DOC adsorped to soil based on initial mass isotherm method. Three replicates and the mean value are shown for each land use. Error bars are standard deviation. Note different scale compared to %BDOC figures.

Table 10. Significant correlations between soil SAR and other soil parameters.

	pH	EC	DOC	Na^+	Land use	m	b	RSP	DOC_{eq}
r	0.66	0.55	0.57	0.83	0.44	0.51	0.54	0.57	0.53
p	< 0.001	0.001	0.003	<0.001	0.003	0.01	0.01	0.003	0.01

Table 11. Significant correlations between soil pH and adsorption parameters.

	m	b	RSP	DOC_{eq}
r	0.54	0.70	0.67	0.68
p	0.01	<0.001	<0.001	<0.001

Synthesis of sources and fates of DOC

A holistic analysis was conducted to determine the relative importance of each of the various processes in the movement of organic carbon through the watershed. Percentages were calculated based on proportions of each land use within the watershed and summed. The resulting pie graphs show that carbon moves similarly through all watersheds in the study (Figure 50). Vegetation BDOC was not included in this analysis as the process is not as likely to occur in natural systems.

Between 31 and 38% of DOC entering the soil is biodegraded by soil microbes and either immobilized or mineralized. Between 5 and 8% of the DOC derived from above ground vegetation is retained in soils at a depth of 0-15cm through adsorption to soil minerals. The remainder, between 55 and 64%, runs off to surface waters. In streams, 3-7% of DOC is biodegraded by stream microbes, which leaves a net stream DOC between 52-57% of the initial DOC input into the system.

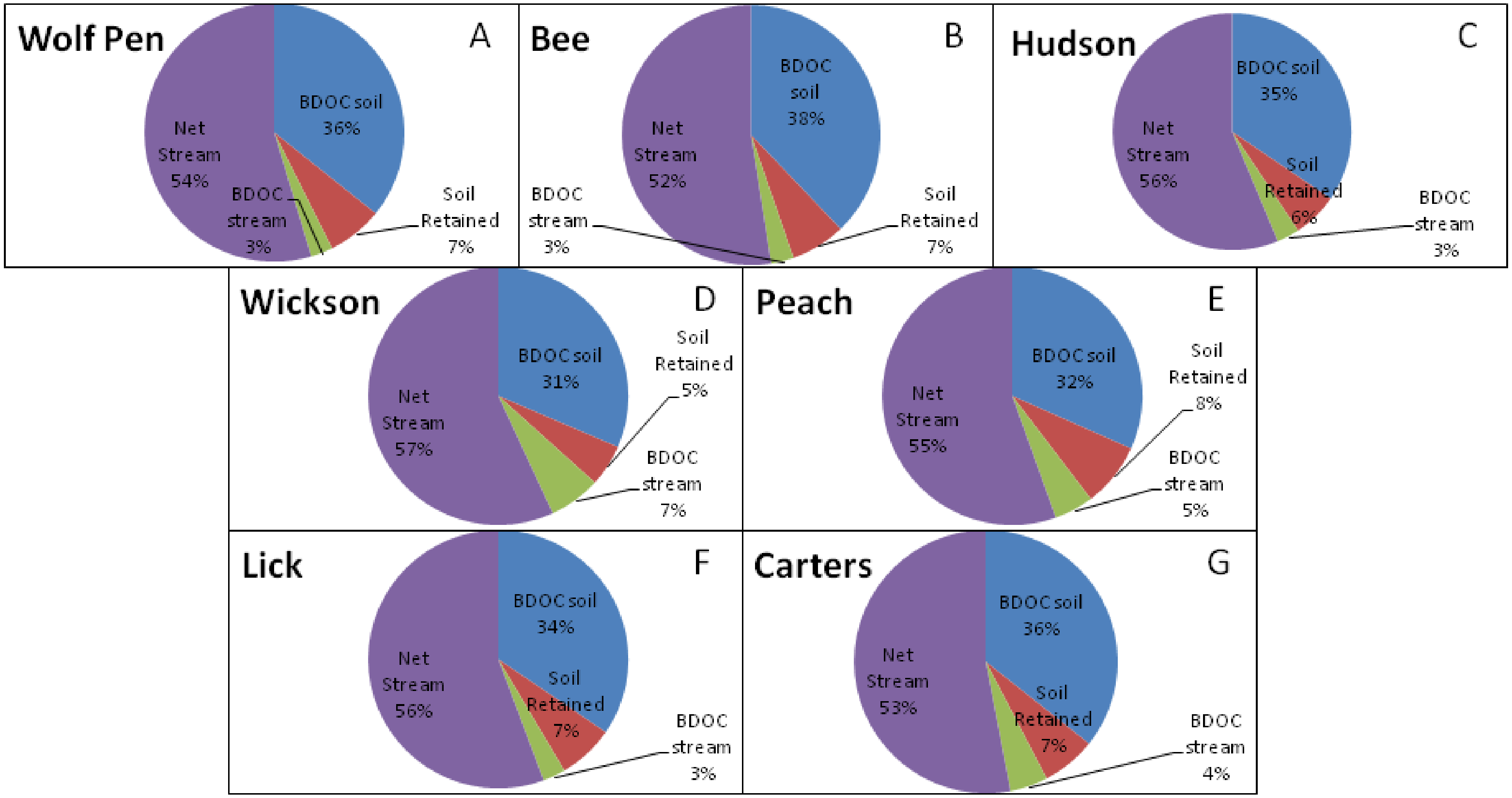

Figure 50. Pie graphs showing how dissolved organic carbon is allocated within each study watershed.

DISCUSSION

Much of the earlier work on the sources and fates of DOC in soils and surface waters focused on small watersheds with little variation in land use (Moeller et al. 1973; Naiman 1982; Downes et al. 1986; Tipping et al. 1988). Previous questions focused on the source and associated molecular structure of DOC (Meyer and O'Hop 1983; David and Vance 1991; Aitkenhead et al. 1999). While some of those questions have been answered over the years, such as that wetlands and peat lands provide the major source of aquatic DOC (Heikkinen 1994; Aitkenhead et al. 1999; Aitkenhead and McDowell 2000), more questions have evolved regarding DOC source and fate.

Recent scientific interest in watersheds with varied land use, particularly those with urban regions, has been shown by biogeochemists examining DOC in soils and streams (Hook and Yeakley 2005; Williams et al. 2005; Aitkenhead-Peterson et al. 2009; Pannkuk et al. 2011; Petrone et al. 2011; Kalscheur et al. 2012; Steele and Aitkenhead-Peterson 2012a, 2012b). The largest contributors to DOC in surface water are waste water effluent (Westerhoff and Anning 2000; Sickman et al. 2007), stormwater runoff especially from urban areas (Hope et al. 2004; Sickman et al. 2007), and more recently, soil exposure to water with high sodium concentrations (Green et al. 2008, 2009; Aitkenhead-Peterson et al. 2009; Steele and Aitkenhead-Peterson 2012b). Development activities within the watershed are also important, as a study utilizing radiocarbon dating in water samples from the Sacramento and San Joaquin Rivers in California suggested that DOC losses from soil can continue for decades after the initial disturbance (Sickman et al. 2010). Watersheds with urban land use have a larger proportion of impervious surfaces, and therefore the volume of runoff is much higher (Hook and Yeakley 2005), causing flashy streams that are prone to stream bank erosion. There are several models to assess stormwater quantity and quality, but the models have a great deal of uncertainty and limits (Dotto et al. 2012).

The Soil Conservation Service (SCS) Runoff Curve Number (RCN) Method

The RCN Method of modeling runoff supported the suggestion that there would be greater runoff at more urbanized watersheds due to an increase in impervious surfaces

(Hook and Yeakley 2005). Current land use data would be helpful to determine distinct curve numbers for Hudson and Lick Creeks, which had the same composite curve number in the analysis for my study. Based on 2006 land use data, Hudson Creek should have more runoff due to greater urban area, and thus impervious surfaces, than Lick Creek watershed.

It is interesting to note that when there is a very small amount of rain (about 0.25 inches), the model shows direct runoff. This may be due to the dominance of HSG Group D soils in the region which have a very low infiltration rate and high runoff potential (Barfield et al. 1981; NRCS 1986). Small amounts of rain may initially runoff of land surfaces as it is difficult for the water to permeate the soil, particularly after a dry spell when soil tends to become hydrophobic. With a precipitation event of 0.25 inches to 0.75 inches, there was very little to no runoff, presumably due to increased rates of infiltration into land surfaces as the precipitation has time to soak into the ground or be intercepted by vegetation. From 0.75 inches of precipitation and higher, runoff increases directly with precipitation, indicating the start of saturation of permeable surfaces.

Sources of dissolved organic carbon in rural and urban watersheds

Current methods for examining the sources of DOC in watersheds include regression analysis, neural networks, and fluorescence. Regression analysis uses a number of watersheds with a range of a certain land use (typically wetlands or peat lands) and quantifies DOC by the strength of the relationship with the chosen land use. Regression is a popular analytical technique because the method is relatively simple (Aitkenhead et al. 1999; Aikenhead-Peterson et al. 2005, 2009). Regression analysis is limited by the fact that there is often a lag in land use data availability, which may be significant if the watershed is undergoing land conversion and development. Co-correlations between land uses may occur, which complicates the quantification and interpretation of DOC concentrations in streamwater (Aitkenhead-Peterson et al. 2009). Neural networks can incorporate a large number of variables in an attempt to model complex systems (Aitkenhead et al. 2007) and have been used by a number of researchers (Clair and Ehrman 1998; Aitkenhead et al. 2007; Kalin and Isik 2010).

However, the addition of more variables increases the error within the model, especially in small watersheds (Aitkenhead et al. 2007). The data collection process can be cumbersome and time consuming due to the inclusion of numerous variables. Fluorescence has been used to track the origin of DOM as from microbes or vegetation (McKnight et al. 2001; Hood et al. 2003; Spencer et al. 2010), but it is less helpful in understanding the spatial variability of DOC within watersheds. There is room for improvement in methodologies to provide a more comprehensive understanding of DOC, especially in watersheds with mixed land uses. The preliminary use of DR-NIR and the resulting WSSL models to track sources of DOC in my study suggested that there is great potential in using DR-NIR as a tool to model DOC contributions from watersheds to streams.

Diffuse reflectance near infrared spectroscopy

The use of DR-NIR spectroscopy to identify non point source inputs of particulate matter and seston to surface waters appears to be a promising tool (Sousa et al. 2007; Martinez-Carreras et al. 2010). The resolution or extent of this type of analysis is unknown at the larger basin size when examining streams and rivers. My study examined the full spectral signature (415nm to 2440 nm) of watershed source inputs of organic material, as well as the spectra of receiving stream waters. At a larger watershed scale, the amount of data input into the WSSL may be too time consuming to collect. There is also likely to be a greater heterogeneous mix of source materials which would make source tracking of organic material more challenging. Further work using a nested stream approach will be used to test this method in future studies. It was assumed that the method could be used on a regional basis and act as a predictive model for all the watersheds in my study, but the difference in geology and irrigation water in the Wickson and Peach watersheds and geology in Lick Creek watershed suggested that this was not possible. For example, in early iterations of the model, the tap water signature was evident in Wickson Creek stream water. However, municipal tap water in the Wickson Creek watershed has decreased levels of sodium and bicarbonate compared to the rest of the B/CS study region. Therefore, the tap water signature seen for Wickson

Creek is unlikely to be an irrigation runoff source. Instead, it appeared that there was an unaccounted source of sodium in the Wickson Creek watershed. Additionally, most of the soil and vegetation samples were taken in the Bee Creek watershed and were aimed at representing different land use types rather than collecting samples from each land use type from every watershed. Future work should be watershed specific in order to have the greatest accuracy possible.

Earlier work suggested that streams with a WTTP upstream will have the signature of effluent and irrigation runoff during dry seasons, while streams without a WWTP will show the signature of only irrigation runoff (Aitkenhead-Peterson et al. 2009). However, the effluent signature was seen in all streams, not just those with a WWTP in the watershed. One possible explanation is that some of the effluent samples clustered with impervious runoff (group 5) which indicates that in some cases, effluent had a different signature that was similar to impervious runoff. There may be seasonal implications involved, as the population of the B/CS region decreases considerably during the summers and holidays due to a high student population, which may have allowed for a more dilute signature in effluent. Future studies would benefit from a range of impervious runoff samples in regards to surface, flow, and time of collection after first flush to better ascertain the relationship between effluent and impervious runoff. It is also possible that the effluent signature may be from failing on-site sewage facilities (OSSFs) in the rural regions. In the Carters Creek watershed alone, 455 OSSFs are estimated to exist (Millican and Hauck 2011). Aging water infrastructure, such as cracks in pipes, might also allow for inputs of effluent like material to streams. While there was some correlation between effluent and animal and bird feces ($r = 0.38$ and $r = 0.50$), it is unlikely that the effluent signature would be confused for other fecal material in spectra analysis.

The amount of variance in stream water chemistry explained by domestic animal feces (dog, pigeon, chicken, and cow) and wild animal feces (cliff swallow) was unexpected. Cliff swallows (*Petrochelidon pyrrhonota*) start building their mud nests on homes, businesses, and bridges over streams as early as mid March and migrate back to

South America as late as September (Gorenzel and Salmon 2008). Cliff swallows are well known for building nests on bridges in Texas; as expressed in an article in the San Angelo Standard-Times, "…if you build a bridge, cliff swallows will come" (Maxwell 2008). Cliff swallows live in large colonies with up to several hundreds of pairs at one site (Gorenzel and Salmon 2008). Typically, cliff swallow feces explained slightly more variance than any other source input of DOM in stream spectra, suggesting that their fecal material either dropped directly into streams from nests under bridges or washed off impervious surfaces via irrigation or stormwater. Cliff swallow fecal material contributed considerably to the DOM loading of the study streams and only slightly more than other animal feces. There are high populations of farms animals in Brazos County as 2007 estimates included 54,735 cattle, 3,395 horses, 1,461 goats, and 778 pigs, as well as 74 poultry farms (USDA 2007). Feral hogs are also present in the region, with an extrapolated estimate of 237-509 in Carters Creek watershed, with presumably higher numbers in rural watersheds (TCEQ 2011). Additionally, as of 2011, there were an estimated 5,218 dogs and 5,887 cats within the urban portion of Carters Creek watershed alone (Millican and Hauck 2011). Considering the number of animals in the region, the high contribution of fecal material to DOC in streams is not surprising.

The spectral signature for impervious runoff was moderately to highly correlated with fecal material ($r = 0.64$ to 0.68 and $r = 0.75$ to 0.82), which suggests that fecal material in the watershed was carried to streams via irrigation and stormwater runoff. Fecal material from wild birds, such as the cliff swallow and the common and great tailed grackle (*Quiscalus quiscula L.* and *Quiscalus mexicanu)*, is ubiquitous in the urban watersheds. The grackles generally roost in large numbers in parking lot trees or overhead power lines where their feces fall directly onto impervious surfaces. Future work would benefit from inclusion of grackle feces in the WSSL model. There are also fecal contributions from dog owners who do not pick up after their pets and from feral cats in the watershed.

Most streams showed soil signatures throughout the sampling period, despite the exceptional drought. Considerable construction activities occurred in most watersheds during the sampling period. The soil signature seen in streams may have been from the wind blowing soil particles onto impervious surfaces where the soil could be flushed into streams by stormwater. However, there was no indication of a strong relationship between impervious runoff (groups 5 and 12) and soils (groups 10 and 15) used in the WSSL models. It is also possible that rain events caused erosion of the stream channel, which may be responsible for the soil signature seen in streams, especially since the streams studied are considered flashy. Soil signatures in stream spectra explained less than 10% of the variance seen in urban stream spectra for the most part, but ranged up to 40% in Wickson Creek, a rural site. High proportions of pasture in this watershed, coupled with the exceptional drought conditions during the sampling period and therefore decreased pasture irrigation, could lead to increased soil exposure as vegetation dies. Peach Creek, the other rural site, did not have as great of an influence by soil. However, Peach Creek was only sampled four times as it was dry in the rest of the sampling period. Therefore, it is difficult to draw comparisons between the two rural sites and future studies would benefit from inclusion of additional rural watersheds to have a more robust data set.

The vegetation signature in the streams varied. Overall, group 6 explained more of the variance in stream spectra than group 8. Group 6 contained more C_3 plant species such as trees, shrubs, and cool season grasses with associated weeds, while group 8 had a greater proportion of C_4 plant species, such as warm season grasses including St. Augustine (*Stenotaphrum secundatum* Walter Kuntze*)*, Bermuda (*Cynodon dactylon* L. Pers*)*, and Centipede (*Eremochloa ophiuroides*) grasses. This observation was supported by carbon isotope analysis, as stream isotope values reflected C_3 vegetation.

The $NaHCO_3$ signature in streams does not necessarily indicate a direct irrigation water source to the stream. Irrigation water can over splash or runoff to impervious surfaces where the water is likely to evaporate quickly on hot impervious surfaces during the Texan summer, leaving salts behind. When a rain event occurs, the salts are carried to streams in stormwater. Accumulated soil sodium is also likely flushed from the soil during rain events. In the rural creeks, baseflow chemistry is likely responsible for the

$NaHCO_3$ signature. Groundwater from both the Cook Mountain formation (Wickson Creek) and Manning formation (Peach Creek) is high in sodium bicarbonate, with bicarbonate values of 225 mg/L in Cook Mountain formation and 137 mg/L in Manning formation (Aitkenhead-Peterson et al. 2011). Sodium adsorption ratio for the Cook Mountain groundwater is 39.9, while SAR is 5.2 for the Manning formation (Aitkenhead-Peterson et al. 2011), illustrating the potential source for the high $NaHCO_3$ water signature seen in rural streams.

The WSSL models were unable to adequately describe Peach and Wickson Creeks, as in most cases a low amount of variance was explained by the WSSL model. This was likely due to inadequate sampling of the source materials of organic matter within these watersheds. Sometimes more than 100% of the variance in a stream was explained by the WSSL model (for example, at urban sites). This suggests that samples specific to each watershed, rather than regional sampling, should be taken as the WSSL database is developed further to create watershed specific WSSLs.

Isotope analysis

Stable carbon isotope analysis can be used to track the source of organic carbon from C_3 or C_4 plants. Isotopic analysis of stream samples indicated that the $\delta^{13}C$ values represented C_3 plants, supporting the findings for source vegetation signature in stream spectra using DR-NIR. The $\delta^{13}C$ values for all samples averaged -24.1‰ while C_3 plants have a $\delta^{13}C$ value of -27‰ and a range from -32 to -22‰ (Boutton 1991; Finlay and Kendall 2007). No sites reported a C_4 plant signature (-16 to -9‰), which supports the findings of other researchers (Schiff et al. 1990; McKnight et al. 2003; Sanderman et al. 2009). However, the three urban sites had the highest $\delta^{13}C$ values which may be reflective of the contribution from C_4 grasses within the watersheds. This may support the hypothesis that urban watersheds will show a greater proportion of impervious runoff and turfgrass signatures (H1), but further isotope analysis is needed to determine if the trend among urban sites is real or an artifact of a small amount of data (N=5 for all sites except Peach Creek where N=2). Additional isotope analysis of ryegrass (*Lolium perenne* L.) used for overseeding, and St. Augustine grass, as well as surveys of the presence of C_3 and C_4 grasses in the sampling region, would be helpful to determine the extent of influence to DOC leaching from these turfgrasses on stream isotope value (Steele and Aitkenhead-Peterson 2012a). Isotope values were negatively correlated to highly developed regions, again possibly reflecting the high amounts of C_4 grasses within the urban regions ($r = -0.80$, $p = 0.03$).

Rural watersheds had significantly lower $\delta^{13}C$ values, perhaps responsive to the forest and shrub scrub vegetation in these regions, while WWTP sites fell in between urban and rural streams, which may be due to mixed vegetation or the influence of human diet in waste water. A study examining the effluent of WWTPs in the Connecticut and Hudson River watersheds reported an average $\delta^{13}C$ value of -26‰ compared to -24‰ in the B/CS region (Griffith et al. 2009). Differences between the studies may be due to sampling design and frequency, as the Griffith study was based on 24 samples from 12 WWTP sites with a variety of treatment size compared to 10 samples in the B/CS region for 2 WWTP sites. Isotope values at WWTP sites may be driven higher than rural sites due to the high prevalence of corn in the human diet, which is a C_4 plant (Griffith et al. 2009).

Wickson Creek had a significantly lower $\delta^{13}C$ value than all sites except Peach Creek. Wickson Creek was observed to have an oily sheen throughout the sampling period which may be due to stormwater runoff or illegal dumping upstream. These additions of oil may be responsible for the lower $\delta^{13}C$ value at Wickson Creek, as oil has a $\delta^{13}C$ value of -30.03‰ (NIST 2012). Evidence of engine oil in Wickson Creek was found using DR-NIR. Between 2 and 12% of the variance in Wickson Creek spectra was explained by engine oil. The largest rain event in the sampling period (February 2012) showed 12% of variance explained by engine oil.

Percent organic carbon provides a relative measure of the portion of organic carbon within a sample. Percent organic carbon did not vary significantly among sites. However, the one rain event analyzed for isotopes (June 2) had a significantly higher percent organic carbon compared to all other sampling periods except January. This is reflective of the flushing effect of precipitation as more organic carbon is mobilized during rain events (Chang and Carlson 2005; Hook and Yeakley 2005). There were no differences in $\delta^{13}C$ based on sampling date.

Carbon isotope values were able to be predicted from the DR-NIR spectra and the resulting cross validation and generation of predicted values were highly and significantly related to observed values. Previously, near infrared spectroscopy has been used to predict many constituents such as lignin, cellulose, and total nitrogen in vegetation (McLellan et al. 1991; Aitkenhead-Peterson et al. 2006; Albrechtova et al. 2008) and clay content, sand, carbon, and total nitrogen in soil as well as soil moisture (Brunet et al. 2008; Zornoza et al.2008). Values for R^2 for soil carbon content reported in the literature range 0.88 to 0.98 (Brunet et al. 2008; Zornoza et al. 2008). Future work should include an increased number of stream sites and corresponding isotope analysis in order to confirm the predictive relationship seen between stream carbon isotope values and DR-NIR stream spectra.

Vegetation extract chemistry

The dominant vegetation of a site will influence DOC concentrations in soil solution and ultimately flux to stream systems (Kuiters 1993). Water extractable DOC (WEDOC) was highest at pasture and developed open sites and was significantly greater than forest and range/shrub scrub areas. The differences seen in WEDOC may be attributable to differences in the type of vegetation at the sites. Based on the data in my study, grass seems to have higher extractable concentrations of carbon compared to shrub vegetation and leaf litter. A study examining the amount of DOC leached from senesced vegetation with solutions with differing SAR found that St. Augustine and ryegrass had higher amounts of leaching under all conditions compared to live oak leaf litter, riparian litter, and mulch (Steele and Aitkenhead-Peterson 2012a). An increase in SAR from 2 to 30 caused a 37-65% increase in the amount of carbon leached from vegetation, which may help to explain the elevated DOC concentrations seen in urban sites. Differences in WEDOC within replicates for each land use may also be attributed to differences in vegetation cover. For example, not every urban open land use (parks) had the same grass species.

Soil extract chemistry

Concentrations of WEDOC in soil solution in my study (17-42 mg/L) compared well to reported results in the literature (5-50mg/L, McDowell and Wood 1984; Zsolnay and Steindl 1991; Herbert and Bertsch 1995). Variation seen in replicates can be attributed to differences in soil chemistry that may be naturally occurring due to differences in litter quantity and quality as well as organic matter content of the soil (Kalbitz et al. 2000).

Sodium plays an important role in the solubilization and transport of DOC in urban watersheds due to irrigation with municipal tap water that is naturally high in sodium and bicarbonate (Aitkenhead-Peterson et al. 2009; Holgate et al. 2011; Pannkuk et al. 2011; Steele and Aitkenhead-Peterson 2012 a,b). It was reported that soil DOC concentrations were highest when equilibrated with sodium compared to calcium and aluminum (Skyllberg and Magnusson 1995). The data reported from the soil extract solutions in my study support the work done by Skyllberg and Magnusson (1995) under forests in Sweden.

Water extractable calcium was significantly higher in urban open areas compared to all other land uses. However, calcium concentration in municipal tap water is relatively low (6 mg/L) compared to in stream concentrations in the B/CS region which range from 24 to 77 mg/L (Aitkenhead-Peterson unpublished data). Additions to soil, such as fertilizer, may have increased the levels of calcium in urban open soils (Steele and Aitkenhead-Peterson 2012b). Alternatively, there may be natural variation of calcium within soils (Steele and Aitkenhead-Peterson 2012b).

A study on urban soils under turfgrass in Texas reported pH values between 7.4-8.6, EC as 570-4570 µs/cm, and SAR as 0.5-9.7 (Steele and Aitkenhead-Peterson 2012b). The data from my study support the work done by Steele and Aitkenhead-Peterson (2012b) in urban areas across Texas. pH data from my study (6.8-9.3) had a greater range than what was reported by Steele and Aitkenhead-Peterson (2012b), but the data were similar. Conductivity in my study was much lower (19-522 µs/cm), but this may be attributed to different methodologies, as Steele and Aitkenhead-Peterson

(2012b) used a soil paste extract method while my conductivity data are from soil solution extracts. Sodium adsorption ratio was lower in my study (0.4-3.9), but within the range reported previously.

Fates of dissolved organic carbon in rural and urban watersheds

DOC biodegradability in vegetation extracts

Few studies have examined BDOC in vegetation. Bulk throughfall from a northern red oak (*Quercus borealis*), red maple (*Acer rubrum*), and paper birch (*Betula papyrifera*) stand in Harvard Forest, Massachusetts, and water extractable spruce litter from a 150 year old Norway spruce (*Picea abies* [L.] Karst.) stand located in the Fichtelgebirge of northeast Bavaria, Germany, were examined in a study quantifying BDOC in vegetation and soils in USA and Europe (McDowell et al. 2006). Spruce litter BDOC averaged 50% while deciduous forest throughfall averaged 35% (McDowell et al. 2006). The percent of DOC lost from St. Augustine grass extract during a 76 hour incubation with effluent ranged from 50-59% compared to a range of 30-53% from leaf litter extract derived from Live Oak (*Quercus fusiformis*) (McCrary et al. in review). Comparatively, the BDOC for vegetation in my study found forest leaf litter averaged 35% and lawn grass, typically composed of a mixture of warm and cool season grasses and weeds, averaged 75%. Forests have lower %BDOC, suggesting that carbon from leaf litter may be more refractory. A previous study in forested headwater streams in North Carolina reported that 30% of daily DOC exports are from leaf litter that has reached streams (Meyer et al. 1998), illustrating the important role of leaf litter as a source of DOC.

DOC biodegradability in soil extracts

Soil solution BDOC has been reported to range from 16-68% (Zsolnay and Steindl 1991; Qualls and Haines 1992; Yano et al. 1998; Andreasson et al. 2009). Studies in forests reported 17-45% BDOC under pine and hardwood trees in soil from Harvard Forest, Massachusetts (Yano et al. 1998), 27% BDOC in a North Carolina oak and hickory forest (Qualls and Haines 1992), and up to 39% BDOC was recorded under beech trees (Andreasson et al. 2009). A study on German agricultural soils found a soil solution BDOC of 16-68% (Zsolnay and Steindl 1991).

Values for soil BDOC in my study were similar to previously published values (19-47% compared to 16-68%). One forest site (John Crompton Park) had very high BDOC compared to the other two replicates. However, all three forest sites have similar DOC concentrations. John Crompton Park is located in a residential neighborhood that consists of mostly apartments and duplexes. A small stream runs through the park and serves as a stormwater channel during rain events. As such, the remnant forest within the park is exposed to stormwater regularly while the other two forest sites are not. The microbial community at this site may differ due to the frequent exposure to stormwater, as differences in soil microbial communities exposed to high sodium irrigation water and grey water have been documented (Holgate et al. 2011). Differences in microbial populations would account for differences in decomposition processes and ultimately BDOC (Andreasson et al. 2009; Holgate et al. 2011). Differences in microbial communities may also explain the decreased BDOC seen for one replicate within each urban land use.

DOC biodegradability in streams

Stream biodegradable organic carbon (BDOC) typically ranges from 4-68% (Wiegner and Seitzinger 2001; Seitzinger et al. 2005; Wiegner et al. 2006). Streams dominated with agricultural and forest land use were reported to have a BDOC of 6-14% (Wiegner and Seitzinger 2001) while values from 4-68% were reported in watersheds with mixed land uses in the east coast of the United States (Seitzinger et al. 2005; Wiegner et al. 2006). Stream BDOC in my study was on the low end of the reported range. Variance was very large for BDOC, with standard deviations ranging from 4.7% at Lick Creek to 9.9% at Hudson Creek. Since the glucose control solution was always degraded above 90% by the inoculant microbes, the stream BDOC data can be considered valid, despite the high variance. The variance may have been due to inconsistent mixing of the stream sample prior to pouring replicates, thus introducing an unbalanced range of refractory and labile molecules. Further work with additional sampling and replication to reduce variability is needed to determine if the pattern of decreasing BDOC from urban to rural areas will continue in different watersheds and at a statistically significant level.

The use of sodium bicarbonate in recarbonation for water treatment purposes decreases BDOC (Zoungrana et al. 1998). In a laboratory study, Zoungrana et al. found little effect when sodium was raised from 3 mg/L to 40 mg/L, but an "important underestimation of BDOC occurred" of 0.4 to 0.6 mg/L when sodium concentration was raised to 109 mg/L. The authors attribute the changes in BDOC to an increase in alkalinity, pH, and sodium concentration. The extremely small increase in BDOC described by Zoungrana et al. (1998) due to high sodium would have made little difference in the BDOC of my study streams in terms of comparison to other stream BDOC studies. Additional analysis of streams for aromaticity would be helpful to understand the extent of refractory compounds in the study streams and confirm the reasons for the low BDOC observed.

Soil adsorption

Previous studies have shown that adsorption of DOC can vary based on land use and land cover (Nodvin et al. 1986; Moore et al. 1992; Riffaldi et al. 1998). The null hypothesis that adsorption of DOC on soil mineral surfaces is the same regardless of land cover ($H0_3$) was not rejected ($\alpha = 0.01$) for the B/CS study region. Differences were shown in release based on a t-test comparing land cover of urban or nonurban ($p = 0.04$), but differences were not seen for adsorption coefficient m ($p = 0.64$), RSP ($p = 0.10$), DOC_{eq} ($p = 0.23$), or percent adsorption ($p = 0.13$).

Soil adsorption as measured through the adsorption coefficient, m, was greatest in wetlands, followed by highly developed and open urban areas. The values for m were on the lower end compared to those from other studies (Nodvin et al. 1986; Moore et al. 1992; Riffaldi et al. 1998; Neff and Asner 2001). Reactive soil pool (RSP), DOC release, and DOC equilibrium values were greatest at highly developed and open urban areas which have exposure to high sodium irrigation water. A positive correlation was found between water extractable soil sodium and RSP ($r = 0.44$, $p = 0.03$). The range reported for reactive soil pool was within values reported by other studies (Nodvin et al. 1986; Moore et al. 1992; Riffaldi et al. 1998; Neff and Asner 2001). Release was highest in an urban open area soccer field (782 mg/kg), compared to the maximum release of 520 mg/kg reported by Moore et al. (1992) in Canadian soils under forests. However, releases up to 780 mg/kg were reported in the A horizon of mollisols (Neff and Asner 2001). Equilibrium DOC (DOC_{eq}) was not significantly different among sites but was within the range reported by other studies (Moore et al. 1992; Moore and Matos 1999). Additional analyses of clay content, soil organic C, aluminum, and iron would be useful in explaining the DOC_{eq} values observed (Moore et al. 1992; Moore and Matos 1999). While percent soil adsorption was not significantly different among sites, percent adsorption was lower at developed open and pasture areas (4 and 5% respectively) compared to an average of 11% at all other sites. Percent adsorption at one wetland site, collected within Lick Creek Park, had a negative percent adsorption due to higher output than input values. This may indicate that the highest concentration used for the Lick Creek wetland sample was too concentrated and breached the adsorption maximum threshold that caused adsorption to decline. Percent adsorption at the next highest concentration averages to 8%.

Exposure to high sodium irrigation water was an important variable in determining soil chemical parameters. While adsorption coefficients were elevated in highly developed and urban open areas, release values were also increased which can be attributed to exposure to high sodium irrigation water (Aitkenhead-Peterson and Cioce in review). Water extractable soil sodium was found to explain the differences seen in RSP (Adj. $R^2 = 0.95$, $p < 0.001$) and release (Adj. $R^2 = 0.94$, $p < 0.001$) through the use of backward multiple regression analysis (Aitkenhead-Peterson and Cioce in review). Direct evidence of irrigation was seen at all urban highly developed sites which were sampled from grass medians in commercial parking lots. Two of the urban open sites were irrigated (Wolf Pen Creek Park and Central Park), but the soccer field at Austin Colony Park was not irrigated, though often exposed to stormwater runoff. Wolf Pen Creek Park was determined to be an outlier due to very low values of release and RSP in addition to water extractable soil sodium as described previously. A similar trend of elevated adsorption coefficient, release, and RSP was seen at one of the urban medium sites, which was the only replicate within the urban medium land use that was irrigated. Urban medium and low sites had adsorption values similar to pasture, range/shrub scrub, and forest soils which indicates that these urban turfgrasses may be lightly managed and functioning similarly to native soils in regards to DOC adsorption (Aitkenhead-Peterson and Cioce in review).

Indigenous carbon and the surface area of soil minerals maximize the amount of DOC adsorped to soil (Moore et al. 1992; Vance and David 1992; McCraken et al. 2002). Exchange sites within the soil at highly developed and urban open areas in my study may be saturated with DOC. It was reported that turfgrass can leach from 4-17% of DOC when exposed to irrigation water with SAR values between 2 and 30 (Steele and Aitkenhead-Peterson 2012a). Comparatively, live oak and riparian leaf litter had lower carbon losses of 2-4% and 3-4% (Steele and Aitkenhead-Peterson 2012a). Therefore, the high percentage of turfgrass at highly developed and urban open sites, coupled with exposure to high sodium irrigation water, may be responsible for increased release of DOC due to saturation with organic matter, allowing a greater reactive soil pool to develop (Aitkenhead-Peterson and Cioce in review). A correlation between percent DOC adsorped to soil and vegetation extract DOC was found ($r = -0.56$, $p = 0.004$), indicating the influence vegetation cover has over soil processes.

High soil solution pH has been shown to decrease DOC adsorption to soil minerals (Kalbitz et al. 2000). Adsorption coefficients for my wetland sites (0.29-0.37) were found to be lower than those seen in another study in China (0.56-0.72) on a natural wetland and a reclaimed wetland which was converted to agricultural land and sampled to a depth of 10 cm (Yu et al. 2010). These differences may be attributed to variation in soil pH, as pH in my study was 1 to 4 units higher than values seen in the Yu et al. (2010) study, and increased pH has been shown to decrease adsorption capacity (Kalbitz et al. 2000; Aitkenhead-Peterson and Cioce in review). However, release was similar between the two studies, ranging from 145-211 mg/kg in the Yu et al. (2000)

study compared to 148-239 mg/kg in my study. The results from my study however did not follow the reported trend of concurrent increases in pH and release of DOC (Whitehead et al. 1981; Hay et al. 1985; Tipping and Hurley 1988; Tipping and Woof 1990; Gödde et al. 1996; Jozefaciuk et al. 1996; Kennedy et al. 1996; Hajnos et al. 1999; You et al. 1999). A number of studies on forests have shown no effect of pH on DOC in regards to fluxes including throughfall, forest floor solutions, and percolates (Chapman et al. 1995; Liechty et al. 1995; Schaaf et al. 1995; Michalzik and Matzner 1999). Kalbitz et al. (2000) have suggested that while there are documented effects of the interactions of pH and DOM in the laboratory, the relationship appears to be minor in the field. In my study, a positive correlation between pH and WEDOC was found ($r = 0.59$, $p = 0.002$) as well as positive correlations between pH and m, b, RSP, and DOC_{eq}.

The adsorption coefficients for forest sites (0.17-0.20) in my study were lower than those reported by Moore et al. (1992) in Canadian soils (0.29 to 0.33 for A horizon soils) assumed to be under forest cover based on the soil series sampled (Aitkenhead-Peterson and Cioce in review). pH values between the studies varied as the Moore et al. (1992) study had an average pH of 3.7 compared to 7.4 in my study (Aitkenhead-Peterson and Cioce in review). Release values and reactive soil pools between these two studies were somewhat similar. Release ranged from 190-320 mg/kg in A horizon soil and RSP was between 270-480 mg/kg in the Moore et al. (1992) study, while release values ranged from 62-264 mg/kg and RSP was between 78-324 mg/kg in my study.

Tropical rainforests and wetlands are regarded as the most productive ecosystems in the world (US EPA 2012c), which may provide similar desirable conditions for ideal microbial growth. Adsorption coefficients from a study in a tropical rainforest ranged from 0.37 to 0.57 (Remington et al. 2007), which were higher than the forest values in my study, but align more closely with my values for wetlands (0.29-0.37). Adsorption coefficients for pasture soils were on the low end of the range reported by Riffaldi et al. (1998) (0.11-0.16 compared to 0.09-0.60). Release values for pasture soils were similar between the Riffaldi et al. (1998) and my data (71-260 mg/kg compared to 14-227 mg/kg) as were pasture reactive soil pools (80-310 mg/kg compared to 65-377 mg/kg).

Clay soils, aluminum, and iron are positively correlated to DOC adsorption in soils (Moore et al. 1992; Nelson et al. 1993; Kalbitz et al 2000). These parameters were not measured in my study. However, most of the soil within the study region is classified as hydrological soil group (HSG) D, which are categorized as clays with a high runoff rate and very low infiltration rate (NRCS 1986). This may indicate that there is potential for increased adsorption within the study region due to the dominance of clay soils. Increased adsorption was not seen in the B/CS region in 2011 compared to other studies (Moore et al. 1992; Riffaldi et al. 1998). However, drought conditions during 2011 may have allowed for increased runoff of DOC due to even lower infiltration in clay soils. Clay soils also shrunk as a result of the drought, making soil sampling to depths greater than 15 cm near impossible.

Temporal changes in soil and stream chemistry in rural and urban watersheds

Temporal changes in soil

The dominant vegetation of a site is important as the litter quality will influence DOC concentrations in soil solution (Kuiters 1993). Variation in soil microbial population and soil structure may also contribute as changes in the microbial community were previously documented after exposure to high sodium municipal tap water (Holgate et al. 2011). Soils exposed to high sodium irrigation water had a two to four times greater loss of dissolved organic carbon compared to soil irrigated with harvested rainwater (Holgate et al. 2011). Evidence of this process can be seen in the data collected at Wolf Pen Creek Park, a developed open site. Soil in the park had a WEDOC concentration of 22 mg/L in 2011 compared to a WEDOC concentration of 30 mg/L in 2010 (Aitkenhead-Peterson and Cioce in review). The two soil samples were collected a year apart and within 1 m^2 of each other. Additionally, water extractable soil sodium was 74 mg/L in 2011 compared to 32 mg/L in 2010. This is a significant increase in soil sodium accumulation (two-tail t-test; $p < 0.05$, Aitkenhead-Peterson and Cioce in review). At Wolf Pen Creek, it appears that chronic exposure to high sodium irrigation water is causing carbon to leach from the soil.

A different relationship occurred at Central Park, another developed open area. Water extractable soil carbon was found to increase at this site. Soil had a WEDOC concentration of 44 mg/L in 2011 compared to 8 mg/L in 2010 (Aitkenhead-Peterson unpublished data). Water extractable soil sodium increased from 5 mg/L in 2010 to 20 mg/L in 2011 (Aitkenhead-Peterson unpublished data). A number of other factors, such as age of the site, vegetation, and use of fertilizer may introduce carbon into the system (Steele and Aitkenhead-Peterson 2012b).

Irrigation water with SAR greater than 5 was shown to cause a two to three times increase in WEDOC in a study examining 33 soils from 26 cities across Texas (Steele and Aitkenhead-Peterson 2012b). Municipal tap water in the region has been recorded well over the established threshold of 5 with reported values of 38.5 in 2010 and 45.2 in 2007 (Aitkenhead-Peterson et al. 2009; Steele and Aitkenhead-Peterson 2012b). Increasing carbon and sodium at Central Park is likely due to interactions with high sodium irrigation water. The trend of decreasing carbon and increasing sodium seen at Wolf Pen Creek is probably due to a threshold of carbon leaching being reached. Green et al. (2008) discuss a “when-it’s-gone-it’s-gone” theory, arguing that high sodium inputs will solubilize DOC and high concentrations of DOC will be leached and ultimately lost with continued sodium exposure. Based on this approach, WEDOC at Wolf Pen Creek should continue to decline and carbon at Central Park should eventually decline due to increased leaching within the soil. Additionally, differences in soil chemistry seen at these two recreational parks may be due to different irrigation regimes. Higher rates of irrigation would increase the intensity of sodium exposure and should ultimately accelerate the “when-it’s-gone-it’s-gone” hypothesis.

Temporal changes in streams

Mean annual DOC concentrations are helpful to understand the natural fluctuation in stream chemistry through the seasons. Mean annual DOC concentrations for my study (March 2011-February 2012) were compared to data collected four years prior on the same streams between March 2007 and February 2008 and limited data collected between March 2010 and February 2011 (Table 12; Aitkenhead-Peterson et al. 2009; Steele and Aitkenhead-Peterson unpublished data). In all cases, DOC decreased over the four year period, ranging from a 3.9% reduction at Peach Creek to 72.2% at Wolf Pen Creek. This decrease in DOC from 2007 to 2011 was significant ($p = 0.02$). pH also significantly increased at all sites ($p < 0.001$), ranging from a 3.8% increase at Hudson Creek to 10.1% at Wickson Creek. The 2010 data mostly follow this decreasing trend. It is important to note that in 2010, Wickson Creek was only sampled 26 times due to construction which made the site inaccessible, while all other sites were sampled 55 times. The summer months, which would typically have the highest DOC concentrations, are not included in the 2010 Wickson Creek data. Therefore, the decrease in DOC seen at Wickson Creek for 2010 is likely an artifact of the incomplete data set. Hudson Creek also had a decrease in DOC for 2010 to 17.6 mg/L relative to 37.3 mg/L in 2007, but increased in the 2011 study to 30.9 mg/L. At the same time, pH increased to 8.7 in 2010 and dropped to 7.9 in 2011. It is possible that this is due to various land management and development activities within the watershed. For example, Miramont Country Club is situated in the headwaters of Hudson Creek and sulfur may be used to lower soil pH on golf course turf (PSU 2003).

Conductivity increased at all sites except Peach and Bee Creeks, ranging from a 15.0% increase at Carters Creek to 39.5% increase at Wickson Creek. Conductivity decreased at Peach and Bee Creeks, at 54.4% and 6.0% respectively. It is important to note that in the 2011 study, Peach Creek was only sampled 4 times as the site was dry for the remaining 10 sampling periods and therefore natural seasonal variation was not captured at Peach Creek. The increase in conductivity was significant if Peach Creek data are excluded ($p = 0.04$).

Previously, increased concentrations of DOC in surface water have been explained by high pH, as humic acids are solubilized at high pH (Stevenson 1994) and a strong correlation was reported between DOC and pH in B/CS streams ($r = 0.81$, $p < 0.01$) (Aitkenhead-Peterson et al. 2009). However, this relationship was not observed in the same region during the 2011 B/CS study (r = -0.19, p = 0.08). It also does not explain the concurrent decreases in DOC and increases in pH seen in data collected for my 2011 study relative to values observed in 2007 (Aitkenhead-Peterson et al. 2009) and concentrations recorded in 2010 (Steele and Aitkenhead-Peterson unpublished data).

Environmental conditions were different during the three sampling periods. Brazos County was under drought conditions for the entire 2011 study as 88% of the sampling period was during "exceptional" drought conditions, the highest intensity of drought as defined by the US Drought Monitor, while the remaining 12% was under "extreme" drought (Fuchs 2012). Comparatively, only 12% of the sampling period in 2007 was during "abnormally dry" conditions, the lowest drought ranking (Fuchs 2012). In 2010, 54% of the sampling period was under some degree of drought (Fuchs 2012).

Precipitation may help explain differences seen in stream DOC concentrations as DOC has been shown to have a positive relationship with flow (Meyer and Tate 1983; Correll et al. 2001; Chang and Carlson 2005; Hook and Yeakley 2005). Precipitation in the region was slightly above average at 1062 mm during the 2007 sampling period compared to 650 mm in 2011 and 745 mm in 2010, which may support lower DOC concentrations in 2011 and 2010 (Aitkenhead-Peterson et al. 2011; NOAA 2012). While changes in flow have been shown to explain 20-45% of variance seen in surface water DOC (Hope et al. 1997), there was no significant relationship between stream DOC and rain events in my study. However, mandatory water restrictions were not imposed in the B/CS region, which may have resulted in more intense irrigation and sodium deposition in soils at some sites.

Changes in precipitation patterns may explain the increases in pH and EC as these parameters have shown to be negatively correlated to stream flow due to the concentration of salts (Wang and Yin 1997). Both WWTP sites had a decrease in DOC over the four year period. Annual discharge records from 2007-2010 indicate that Lick Creek WWTP has steadily increased the amount of discharge over the four years (US EPA 2012b), while Burton Creek WWTP shows a slight decrease in discharge (Figure 51, US EPA 2012a). Increases in flow from WWTPs would typically increase DOC in receiving streams, however, the opposite was reported at Lick Creek which had an 18% increase in discharge. This may be due to the influence of sodium, as described below. The slight 4% decrease seen in Burton WWTP discharges over four years would support the decrease in DOC seen in Carter Creek. It is important to note that discharge data from the WWTPs are not yet publically available for 2011 and flow values may be different due to the exceptional drought seen in 2011.

Exposure to chronic additions of sodium from deicing salts was shown to cause a loss of carbon from soil in Great Britain (Green et al. 2008, 2009). Irrigation with high sodium tap water may also be reducing carbon in soils, thereby decreasing the amount of carbon available to be transported to surface waters. Sodium additions, coupled with a decrease in flow due to drought conditions, may explain the losses seen in surface water DOC and the increases in pH and EC from 2007 to 2011. Previously, DOC concentrations in stream water were linked to SAR (Aitkenhead-Peterson et al. 2009). However, this relationship did not hold for the 2011 study (p = 0.69).

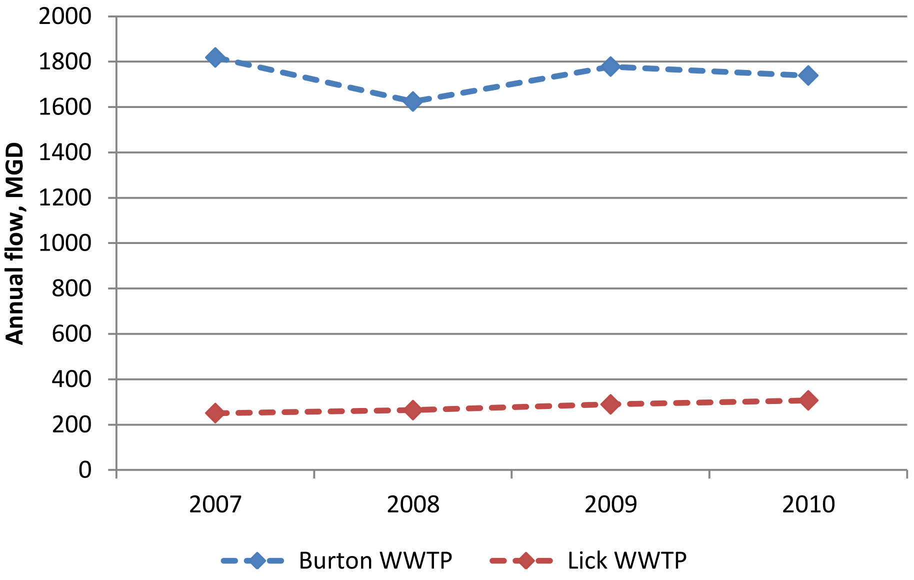

Figure 51. Changes in annual flow (MGD) for Burton and Lick WWTP. 2010 is the most recently available data. Data is from the U.S.EPA’s Enforcement and Compliance History Online (ECHO).

Table 12. Mean annual DOC (mg/L), pH, and EC (µs/cm) for the current study data collected from March 2011-February 2012, unpublished data collected from March 2010-February 2011 (Steele and Aitkenhead-Peterson), and data collected from March 2007-February 2008 (Aitkenhead-Peterson et al. 2009). Percent change in mean annual DOC, pH, and EC over four years (2007 to 2011) is shown.

	DOC mg/L				pH				EC µs/cm			
Stream	Current study 2011	Steele and Aitkenhead-Peterson Unpublished data 2010	Aitkenhead-Peterson et al. 2009	Percent change	Current study 2011	Steele and Aitkenhead-Peterson Unpublished data 2010	Aitkenhead-Peterson et al. 2009	Percent change	Current study 2011	Steele and Aitkenhead-Peterson Unpublished data 2010	Aitkenhead-Peterson et al. 2009	Percent change
Wolf Pen	14.6	14.0	52.5	-72.2	8.5	8.6	8.1	4.4	1262	1406	1005	20.4
Peach	19.6		20.4	-3.9	7.8		7.4	4.9	388		851	-54.4
Lick	11.6		32.2^{+}	-64.1	8.0		7.7$^{\&}$	4.2	994		950$^{\&}$	4.4
Bee	21.2		31.5	-32.7	7.9		7.6	4.3	766		815	-6.0
Wickson	15.5	11.8*	20.5	-24.3	7.8	8.3*	7.0	10.1	609	645*	368	39.5
Hudson	30.9	17.6	37.3	-17.1	7.9	8.7	7.6	3.8	950	840	619	34.9
Carters	11.4	11.5	38.6	-70.4	8.1	8.4	7.7	5.2	1082	977	919	15.0

[+] Lick Creek data is unpublished and did not appear in Aitkenhead-Peterson et al. 2009.

[&] Lick Creek data was published in Aitkenhead-Peterson et al. 2011.

*Wickson Creek data is based on half as many samples as other sites due to construction and site inaccessibility.

Urban open area was correlated to stream DOC concentrations (Aitkenhead-Peterson et al. 2009) in some of the same watersheds used in the 2011 B/CS study. Land use did not explain the stream DOC concentrations in my study. This may be due to the decreases seen in DOC concentration over the last four years as described above. Decreases in DOC concentration may be due to increased levels of soil sodium in some of the urban open area sites. Land use data used in my study were from 2006, which is the most recently available version. The land use data were "ground-truthed" as much as possible, but it is likely that recent developments may not be fully captured in the data. Additionally, the land use data is processed by USGS at a regional scale and only captures features larger than one acre (0.004km^2) (MRLC 2011). A number of important changes in the landscape may have been missed, such as small patches of remnant forest, shrub scrub, or riparian areas, which could be of great importance for understanding the processing of carbon. Additionally, measuring the proportion of humic and fulvic acids in future studies would be valuable in determining how fractions of DOC move between pools.

Synthesis of sources and fates of dissolved organic carbon in rural and urban watersheds

Vegetation plays an important role in regulating DOC in soil solutions as vegetation cover determines the quality of plant debris available as a source of DOC (Kuiters 1993). Vegetation inputs are also sources of DOC directly to streams through litter deposits (Bernhardt and McDowell 2008; Steele and Aitkenhead-Peterson et al. 2012a). Vegetation BDOC was analyzed for these reasons. Vegetation extracts had the least variation of any matrix analyzed for BDOC. Variance in BDOC increased as DOC moved through the watershed, with more variance in soils, and the greatest variance was observed in streams. This may be due to a large labile portion of DOC being biodegraded before reaching waterways. Alternatively, the solubilization of humic acids in soil may have provided a more refractory form of DOC in streams which is resistant to microbial breakdown. The strong vegetation signature quantified by DR-NIR seen in almost all streams suggests that perhaps more refractory compounds from vegetation were present in streams. The data support this, as BDOC decreases through the watershed from an average of 63% in vegetation, 32% in soils, and 6% in streams.

The holistic analysis revealed that stream BDOC is similar among all sites, but slightly higher in rural watersheds. This may be due to a more diverse microbial population at these sites, which have less impact from anthropogenic development, as well as different sources of irrigation water that vary somewhat from the irrigation water chemistry in the rest of the study region. The relative proportion of soil adsorption of DOC (retention) was similar in all watersheds, which suggests that land use does not have an important influence on soil adsorption of DOC. However, analysis of the adsorption terms found that soils in urban regions are compromised in their ability to retain DOC relative to shrub scrub land use (Aitkenhead-Peterson and Cioce in review). In this case, the relative analysis may not show the small, but important, differences in soil adsorption terms. Soil BDOC was lower in rural watersheds compared to urban and WWTP sites, probably due to differences in microbial populations. Microbial community composition has been shown to be affected by differences in irrigation water chemistries such as harvested, grey, and municipal tap waters (Holgate et al. 2011). In all watersheds, greater than 50% of carbon enters the stream based on the holistic synthesis. This is confirmed by DR-NIR analysis of the spectral signatures where between 20% (Wickson) and up to 100% (other streams) of the variance in stream spectral signature is explained by source groups of DOC within the watershed. The holistic analysis was also based on 2006 land use data (the most recently available) and considerable changes in land use probably occurred between 2006 and the sampling period, which are not reflected in the analysis.

Humic acids are typically thought to be more refractory due to their relatively high molecular weight compared to lighter fulvic acids (Tate 1987). Humic acids are also more soluble in higher pH conditions, while fulvic acids are soluble under all pH regimes (Stevenson 1994). In contrast, Boyer and Groffman (1996) reported that humic acids were more bioavailable than fulvic acids in agricultural and forest soils. It has also been suggested that hydrophobicity is a more important control of organic matter rather than its molecular weight (Piccolo 1998). This is based on a theory that humic acids are combinations of small molecules, rather than macromolecules. Piccolo (1998) argued that framing DOM bioavailability based on molecular weight is not appropriate.

It has been suggested that DOC might accumulate in upper soils during low flows and be mobilized to streams during high flows (Boyer et al. 1996). The streams in the study region are flashy and have large changes in flow due to stormwater runoff. This suggests that DOC inputs to waterways may be from discrete events, rather than continuous inputs over time. Other studies have shown the length of soil dryness, ambient temperature, and the fluxes of water are positively correlated to the concentration of DOC released from soil after a dry period (Chittleborough et al. 1992; Tipping et al. 1999). However, a relationship was not found between DOC in rain events and dry periods. It is possible that the first flush from land surfaces was missed due to a lag in sampling after the rain event and increases in DOC were not captured. Flow was not measured in my study and USGS gauge data is not available in the region. It is typically thought that soil adsorption of DOC plays a greater role than decomposition in reducing DOC concentrations in soil (Kalbtiz et al. 2000). Soil BDOC averaged to 35% based on land use, while soil adsorption averaged to 7% in the holistic analysis. The possible saturation of highly developed and urban open soils for DOC and drought conditions resulting in decreased soil infiltration may be contributing to lower adsorption than possible in the urban and rural watersheds studies.

This study also illustrates the impacts of high sodium inputs on the movement of organic carbon through the ecosystem. The use of high sodium irrigation water was intensified by drought conditions as there was less precipitation input to dilute the concentration of sodium, which caused increases in pH and EC. The data indicated that high sodium irrigation water may be reducing carbon in soils, thereby decreasing the amount of carbon available to be transported to surface waters. Sodium additions, coupled with a decrease in flow due to drought conditions, may explain the losses seen in surface water DOC and the increases in pH and EC from 2007 to 2011. Green et al. (2008) discuss a “when-it’s-gone-it’s-gone” theory, and argued that high sodium inputs will cause DOC to become more soluble, but high concentrations of DOC will be leached and ultimately lost with continued sodium exposure. High sodium inputs may also alter the microbial populations in soil, therefore altering processing potential.

Sodium also affected soil adsorption as water extractable soil sodium was correlated to both RSP and release of DOC. The increased percentage of turfgrass at highly developed and urban open sites, coupled with exposure to high sodium irrigation water, may be responsible for increased release of DOC due to saturation with organic matter, allowing a greater reactive soil pool to develop. Impacts can also been seen in the environmental service of carbon sequestration in soil, as soil carbon is more likely to be sequestered under urban turfgrass compared to agricultural soils with conventional tillage (Morgan et al. 2010). High sodium irrigation water may pose a greater risk of leaching of sequestered carbon (Steele and Aitkenhead-Peterson 2012b). It was also suggested that soils high in sodium could function as a nonpoint source of carbon and other nutrients to surface waters (Steele and Aitkenhead-Peterson 2012b). Management strategies, such as total irrigated area and irrigation rates, and soil structure, such as impermeable layers which could cause subsurface lateral flow, could also influence the movement of carbon as a result of high sodium inputs (Steele and Aitkenhead-Peterson 2012b). As shown, sodium is a major driver and control on the movement of DOC in the study region.

Limitations to study

Further DR-NIR analysis using the WSSL should strive to collect source materials of DOM that are watershed specific. Grackle feces, as well as more impervious runoff samples, should be incorporated into the WSSL to provide more accurate results. A survey of the distribution of C_3 and C_4 grasses in the study area would also be useful to understand the role these types of vegetation play in DOC leaching from soil and corresponding stream isotope values. All analyses would benefit from the inclusion of additional rural watersheds in the dataset, since one of the two rural watersheds was dry for the majority of the sampling period and it was difficult to draw comparisons and conclusions.

Changes in sampling design may be beneficial for future studies. Soil and vegetation samples were taken over four different sampling periods, from June 2011 to January 2012. An increase in soil DOC due to rewetting after dry periods has been well documented (McDowell and Wood 1984; Zabowski and Ugolini 1990; Haynes and Swift 1991; Chittleborough et al. 1992; Kalbitz and Knappe 1997; Lundquist et al. 1999; Tipping et al. 1999; Zsolnay et al. 1999). This phenomenon may have contributed to variance in the samples, especially because most of the sampling period was during exceptional drought. Soil moisture conditions may have changed among soil sampling periods. Future studies would benefit from collecting samples within a single sampling period to limit influences from soil moisture, changes in microbial community, and seasonality, especially for vegetation. Additionally analyses of percent clay and aluminum and iron content would be useful for delineating trends in the adsorption study and allowing for better comparison with other research.

Lastly, analysis of aromaticity and the proportion of humic and fulvic acids in streams would help to answer questions about how DOC moves through the watershed and the extent of refractory DOC present in the study region.

CONCLUSIONS

The first null hypothesis ($H0_1$) that the source of DOC in each watershed would be the same regardless of land cover and land use was not rejected. Limited isotope data, combined with preliminary WSSL models, did not generate enough data to conclusively reject this hypothesis. Isotope data did show significantly different carbon isotope values at rural sites compared to urban and WWTP streams ($p < 0.001$, $\alpha = 0.05$). Isotope data might also suggest that urban watersheds will show a greater proportion of impervious runoff and turfgrass signatures as the urban sites had the highest $\delta^{13}C$ values, which may be reflective of high amounts of C_4 grasses within the watersheds. This is complicated by the fact that C_3 and C_4 plants have shown different levels of DOC leaching when exposed to high sodium water, and two of the common turfgrasses in the region seem to leach carbon differently (Steele and Aitkenhead-Peterson et al. 2012a). The WSSL models are challenging to interpret for this hypothesis as the models were designed subjectively. The 100% stacked column figures, which give a relative sense of source material contribution in each watershed over the sampling period, show variety in source over time, but there are not any obvious differences in urban streams compared to rural and WWTP sites.

The second null hypothesis was split into two parts. The first hypothesis, that there would be no significant difference in stream BDOC according to land use ($H0_{2a}$), was not rejected. Biodegradable BDOC was not found to be higher in watersheds with less urban land use and in watersheds with WWTP due to a young, more labile, source of DOC as initially thought. No significant difference in BDOC in streams was reported ($p = 0.06$, $\alpha = 0.01$), though BDOC did increase from urban to rural watersheds. Additional analyses are needed to determine if this trend is valid. The second hypothesis, that there would be no significant difference in soil BDOC based on land use ($H0_{2b}$) was not rejected ($p=0.80$, $\alpha = 0.05$). There were no significant differences in soil BDOC based on land use.

The third null hypothesis that adsorption of DOC on soil mineral surface is the same regardless of land cover ($H0_3$) was not rejected ($\alpha = 0.01$). While differences were shown based on the release term (b, $p = 0.04$), no differences were seen based on the adsorption coefficient (m, $p = 0.64$), RSP ($p = 0.10$), DOC_{eq} ($p = 0.23$), or percent adsorption ($p = 0.13$).

Based on the hypotheses outlined above, useful trends for future studies or land use management were seen in regards to the sources and fates of DOC in rural and urban watersheds:

1. Stream spectra may be able to predict carbon isotope values in streams. Regression analysis found an adjusted R^2 of 0.88 for predicted $\delta^{13}C$ ‰ values based on DR-NIR stream spectra compared with observed $\delta^{13}C$ ‰ values. Additional analysis is needed to confirm this observation.
2. Preliminary WSSL models seem promising as a method to examine the source of carbon in streams, but further work is needed to develop watershed specific WSSLs based on source inputs of organic material within the watershed of interest. Cliff swallows had a considerable impact on DOM loading in B/CS streams.
3. Concentrations of DOC in B/CS streams decreased between 2007 and 2011, while pH and EC increased. Additions of sodium from high sodium irrigation tap water, combined with decreased precipitation during the exceptional drought in 2011, may have caused decreased carbon in soils following the "when it's gone it's gone hypothesis" which is also supported by recent work that SAR values greater than 5 will increase the amount of DOC leaching from soils. These factors act to decrease the amount of carbon that can be transported to surface waters.
4. Biodegradable DOC was low in streams, which is likely due to DOC being present in streams in refractory forms that are resistant to microbial breakdown, as the labile portion of DOC is degraded before reaching waterways. The data

support this, as BDOC decreases through the watershed from an average of 63% in vegetation, to 32% in soils, and 6% in streams.

5. Soil chemistry, including soil adsorption, was greatly influenced by sodium. Water extractable soil sodium was correlated to both RSP and release of DOC, as well as Mg, Ca, SAR, pH, EC, and water extractable DOC. The elevated adsorption coefficients and release values seen in highly developed and urban open areas can be attributed to frequent exposure to high sodium irrigation water.

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APPENDIX A

MEAN WATER CHEMISTRY DATA AND STANDARD DEVIATIONS FOR STREAM SAMPLES COLLECTED BETWEEN MARCH 2011 AND FEBRUARY 2012.

Date	Site	DOC mg/L	% BDOC	pH	EC µS/cm
3/4/2011	Bee	12±2	13±2	7.8	794
4/11/2011	Bee	23±2	4±7	8.3	1282
5/13/2011	Bee	22±1	3±6	7.1	490
6/8/2011	Bee	21±1	2±3	8.2	793
6/22/2011	Bee	19±0	8±9	7.9	178
7/1/2011	Bee	23±2	1±2	8.0	858
8/2/2011	Bee	29±3	5±6	8.4	1578
9/6/2011	Bee	40±1	10±4	8.1	1087
9/19/2011	Bee	18±0	12±3	7.9	358
10/5/2011	Bee	20±2	0	8.3	830
11/10/2011	Bee	22±1	0	8.0	859
12/3/2011	Bee	21±0	0	8.0	608
1/16/2012	Bee	16±1	5±8	7.1	574
2/6/2012	Bee	12±0	9±2	7.9	439
3/4/2011	Carters	12±0	19±3	7.8	1051
4/11/2011	Carters	10±0	6±2	7.8	1354
5/13/2011	Carters	16±2	1±1	7.7	692
6/8/2011	Carters	11±0	13±8	8.3	1323
6/22/2011	Carters	17±1	14±9	8.0	333
7/1/2011	Carters	8±0	2±2	8.2	1487
8/2/2011	Carters	9±2	11±16	8.2	1455
9/6/2011	Carters	10±0	23±15	8.2	1427
9/19/2011	Carters	17±1	1±1	8.2	521
10/5/2011	Carters	8±2	2±4	8.5	1368
11/10/2011	Carters	8±2	0	8.8	1061
12/3/2011	Carters	11±2	8±13	8.1	1290
1/16/2012	Carters	10±2	7±2	8.0	1308
2/6/2012	Carters	12±0	6±3	7.9	473
3/4/2011	Hudson	21±2	0	8.0	651

4/11/2011	Hudson	18±1	4±2	8.1	976
5/13/2011	Hudson	28±1	20±17	7.6	820
6/8/2011	Hudson	30±1	0	7.7	1009
6/22/2011	Hudson	36±5	0	7.9	440
7/1/2011	Hudson	34±2	1±2	8.1	1277
8/2/2011	Hudson	52±4	2±4	8.5	1818
9/6/2011	Hudson	46±3	1±1	8.4	1500
9/19/2011	Hudson	42±0	5±7	8.1	768
10/5/2011	Hudson	34±4	0	7.7	1467
11/10/2011	Hudson	19±2	2±3	8.1	766
12/3/2011	Hudson	18±3	35±12	8.1	788
1/16/2012	Hudson	43±1	2±3	6.5	701
2/6/2012	Hudson	13±0	1±1	7.9	321
3/4/2011	Lick	10±0	0	7.9	908
4/11/2011	Lick	10±0	10±12	7.5	1238
5/13/2011	Lick	19±1	4±3	7.1	407
6/8/2011	Lick	8±0	7±9	8.2	1324
6/22/2011	Lick	17±0	0	7.8	437
7/1/2011	Lick	8±0	1±1	8.0	1206
8/2/2011	Lick	8±1	0.4±0	8.4	1340
9/6/2011	Lick	9±1	6±9	8.4	1236
9/19/2011	Lick	15±0	6±10	7.8	1230
10/5/2011	Lick	8±2	2±4	8.6	1222
11/10/2011	Lick	15±2	1±2	8.1	835
12/3/2011	Lick	15±0	16±4	8.2	973
1/16/2012	Lick	10±1	4±4.7	8.6	1057
2/6/2012	Lick	12±0	10±5	8.0	506
3/4/2011	Peach	31±2	0	7.6	634
4/11/2011	Peach	dry	dry	dry	dry
5/13/2011	Peach	dry	dry	dry	dry
6/8/2011	Peach	dry	dry	dry	dry
6/22/2011	Peach	15±1	15±3	7.7	197
7/1/2011	Peach	dry	dry	dry	dry
8/2/2011	Peach	dry	dry	dry	dry
9/6/2011	Peach	dry	dry	dry	dry
9/19/2011	Peach	dry	dry	dry	dry
10/5/2011	Peach	dry	dry	dry	dry
11/10/2011	Peach	dry	dry	dry	dry

12/3/2011	Peach	Dry	dry	dry	dry
1/16/2012	Peach	20±5	10±4	7.9	405
2/6/2012	Peach	13±1	7±1	7.9	315
3/4/2011	Wickson	17±2	21±2	7.7	308
4/11/2011	Wickson	18±1	11±2	7.7	561
5/13/2011	Wickson	15±1	6±2	7.1	722
6/8/2011	Wickson	9±1	2±1	8.5	895
6/22/2011	Wickson	12±0	8±10	7.7	840
7/1/2011	Wickson	17±1	6±2	7.4	548
8/2/2011	Wickson	18±1	9±7	7.6	637
9/6/2011	Wickson	17±1	6±5	8.0	682
9/19/2011	Wickson	21±0	19±5	7.8	748
10/5/2011	Wickson	Dry	dry	dry	dry
11/10/2011	Wickson	17±1	2±4	7.8	677
12/3/2011	Wickson	16±1	21±19	7.8	783
1/16/2012	Wickson	15±1	8±1	8.3	373
2/6/2012	Wickson	11±0	13±6	8.1	139
3/4/2011	Wolf Pen	8±1	0	7.9	1205
4/11/2011	Wolf Pen	17±4	16±12	8.8	1180
5/13/2011	Wolf Pen	17±1	0.4±1	6.8	387
6/8/2011	Wolf Pen	17±2	5±9	9.0	1614
6/22/2011	Wolf Pen	19±2	0	7.9	199
7/1/2011	Wolf Pen	12±3	10±17	9.3	2080
8/2/2011	Wolf Pen	12±2	5±8	9.1	1677
9/6/2011	Wolf Pen	16±1	0	8.9	1990
9/19/2011	Wolf Pen	16±1	6±5	8.4	333
10/5/2011	Wolf Pen	10±3	0	9.0	1839
11/10/2011	Wolf Pen	15±3	9±16	8.9	1491
12/3/2011	Wolf Pen	20±1	4±5	8.4	1559
1/16/2012	Wolf Pen	15±4	0	8.5	1487
2/6/2012	Wolf Pen	13±1	12±7	7.8	626

APPENDIX B

MEAN SOIL CHEMISTRY DATA AND STANDARD DEVIATIONS.

Land use classification	Site	Soil:Solution ratio	Soil g	DDW g	pH	EC µS/cm	Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	SAR
Developed High	Post Oak Mall	10.0	9.1	90.3	10.0±0.2	114±88	20±2	6±1	6±1	1±0	3.3±0.1
Developed High	College Station Target	10.0	9.0	90.1	8.4±0.4	62±21	12±0	4±1	2±1	0.2±0	3.6±0.6
Developed High	Bryan HEB	9.9	9.1	90.4	9.5±0.2	138±3	30±1	1±0.2	7±0	0.8±0	4.1±0.2
Developed Medium	908A Azalea	10.0	9.1	90.6	7.5±0.3	150±14	5±0	3±1	9±3	2±1	0.6±0.1
Developed Medium	Woodsman Dr	10.0	9.1	90.4	8.3±0	48±3	10±0	12±1	5±1	0.7±0	1.4±0
Developed Medium	Renaissance Park Apts	10.0	9.1	90.6	7.6±0.3	53±12	10±0	5±1	2±0	0.3±0	2.4±0.1
Developed Low	800 Marion Pugh	9.9	9.1	90.1	7.5±0.2	37±3	6±2	3±0	2±0	0.3±0	1.5±0.4
Developed Low	Lawyer St	9.9	9.1	90.1	8.0±0.1	44±2	5±2	2±1	3±0	0.4±0.7	1.1±0.2
Developed Low	Haines St	10.0	9.1	90.3	7.6±0	50±4	11±5	2±1	2±1	0.3±0.1	3.7±2.9
Developed Open	Central Park	9.9	9.1	90.7	9.2±0	76±6	20±2	2±1	8±1	1±0.1	2.5±0.1
Developed Open	Wolf Pen Creek Park	10.0	9.0	90.4	7.2±0.2	1181±14	74±2	3±0	23±2	7±0.1	4.9±0.1
Developed Open	Austin Colony soccer field	9.8	9.2	90.4	10.2±0.2	309±5	58±16	4±2	14±0	2±0.2	5.4±1.1
Forest	John Crompton Park	9.8	9.2	90.7	8.0±0.5	26±7	6±3	5±1	3±1	0.4±0.2	1.3±0.3
Forest	Lick Creek Park	10.0	9.1	90.6	6.7±0.1	58±59	7±0	5±6	2±0	0.5±0	1.7±0.1
Forest	Kathy Fleming	9.9	9.2	90.4	7.5±0.2	45±1	1±0	3±0	5±0	0.9±0	0.1±0
Pasture	Kathy Fleming	9.9	9.2	90.4	6.8±0.2	39±19	2±1	4±2	5±3	0.5±0.2	0.3±0.2
Pasture	Wilcox Rd	9.8	9.2	90.5	7.3±0.1	27±7	1±0	2±0	2±0	0.3±0.2	0.3±0

Pasture	N Country Estates	9.9	9.1	90.4	6.2±0.1	22±1	3±3	4±2	2±1	0.4±0	0.6±0.5
Range/SS	Briarcrest and Woodcrest	9.9	9.1	90.4	9.3±0.2	23±4	7±0	1±0	1±0	0.2±0	2.6±0
Range/SS	Old Ti Rd	9.9	9.2	91.3	6.5±0	9±5	1±0	3±1	1±0	0.1±0	0.4±0.4
Range/SS	Miramont	9.8	9.1	90.2	6.5±0	24±4	3±0	2±1	1±0	0.1±0	0.9±0.1
Wetland	Copperfield	10.0	9.1	90.4	8.6±0.7	6±3	10±2	13±12	3±1	0.5±0.2	3.0±0.9
Wetland	Austin Colony Park	9.9	9.2	90.5	7.4±0.2	43±11	6±0	2±0	5±0.5	0.6±0	1.0±0.1
Wetland	Lick Creek Park	9.9	9.1	90.5	6.8±0.5	25±4	5±3	10±8	2±1	0.3±0.1	1.2±0.5

APPENDIX C

SOIL AND VEGETATION DOC AND % BDOC

Land use classification	Site	WEDOC Soil mg/L	% BDOC Soil	WEDOC vegetation mg/L	% BDOC vegetation
Developed High	Post Oak Mall	55±4	5±3	334±4	73±2
Developed High	College Station Target	23±1	29±16	498±6	73±2
Developed High	Bryan HEB	48±1	23±5	538±8	71±1
Developed Medium	908A Azalea	16±1	15±2	345±7	66±1
Developed Medium	Woodsman Dr	13±1	61±1	617±5	69±2
Developed Medium	Renaissance Park Apts	49±3	64±1	861±10	74±1
Developed Low	800 Marion Pugh	28±1	49±3	963±6	75±0
Developed Low	Lawyer St	8±1	7±24	341±3	79±2
Developed Low	Haines St	16±1	66±1	544±4	72±1
Developed Open	Central Park	44±3	44±2	788±10	55±24
Developed Open	Wolf Pen Creek Park	22±2	50±11	872±4	73±2
Developed Open	Austin Colony soccer field	82±2	15±15	699±3	65±6
Forest	John Crompton Park	28±1	77±1	272±17	37±2
Forest	Lick Creek Park	17±1	24±13	111±2	31±2
Forest	Kathy Fleming	20±1	13±5	256±3	34±21
Pasture	Kathy Fleming	18±2	34±3	837±9	78±2
Pasture	Wilcox Rd	16±3	19±3	840±8	64±3
Pasture	N Country Estates	44±3	37±4	722±3	75±1
Range/SS	Briarcrest and Woodcrest	20±1	33±4	247±12	68±0
Range/SS	Old Ti Rd	10±1	40±4	312±7	46±2
Range/SS	Miramont	26±1	18±4	256±2	55±1
Wetland	Copperfield	37±3	12±2	305±4	58±2
Wetland	Austin Colony Park	20±1	22±2	211±3	48±3
Wetland	Lick Creek Park	29±1	23±5	623±7	63±2

APPENDIX D

GLUCOSE CONTROL FOR BIODEGRADBILITY STUDIES

Date	% BDOC
3/4/2011	91.7±0.8
4/11/2011	94.3±0.6
5/13/2011	93.4±0.7
6/8/2011	91.4±1.0
6/22/2011	93.5±1.0
7/1/2011	94.1±0.8
8/2/2011	93.8±1.6
9/6/2011	98.9±0.2
9/19/2011	92.1±3.1
10/5/2011	90.8±0.3
11/10/2011	91.9±2.2
11/27/2011	94.4±1.3
12/3/2011	99.8±7.0
1/19/2012	94.6±2.1
1/26/2012	92.2±3.9
2/3/2012	93.0±0.3
2/15/2012	93.3±0
2/23/2012	91.3±0.4
2/26/2012	92.5±0.5

APPENDIX E

SOIL ADSORPTION

Land use classification	Site	R^2	m	b mg/kg	RSP mg/kg	DOC_{eq} mg/L
Developed High	Post Oak Mall	0.91	0.35±0.08	587±31	607±538	177±24
Developed High	College Station Target	0.92	0.25±0.05	305±46	409±88	125±7
Developed High	Bryan HEB	0.98	0.26±0.03	346±24	469±48	130±7
Developed Medium	908A Azalea	0.98	0.19±0.02	89±62	111±79	24±24
Developed Medium	Woodsman Dr	0.93	0.20±0.01	97±6	121±10	49±0.1
Developed Medium	Renaissance Park Apts	0.81	0.26±0.01	228±14	308±16	90±9
Developed Low	800 Marion Pugh	0.89	0.17±0.06	195±48	238±76	115±10
Developed Low	Lawyer St	0.88	0.21±0.07	128±44	165±70	62±2
Developed Low	Haines St	0.82	0.20±0.03	216±29	272±46	106±1
Developed Open	Central Park	0.94	0.27±0.09	433±31	599±116	169±48
Developed Open	Wolf Pen Creek Park	0.93	0.17±0.03	10±6	12±8	7±2
Developed Open	Austin Colony soccer field	0.90	0.41±0.01	782±25	1330±23	194±4
Forest	John Crompton Park	0.90	0.18±0.07	264±12	324±43	161±61
Forest	Lick Creek Park	0.96	0.20±0	62±9	78±12	32±4
Forest	Kathy Fleming	0.92	0.17±0.02	195±25	236±35	115±4
Pasture	Kathy Fleming	0.84	0.13±0.02	127±14	146±20	97±4
Pasture	Wilcox Rd	0.96	0.11±0.03	71±41	80±49	61±19
Pasture	N Country Estates	0.72	0.16±0.03	260±33	310±49	164±8
Range/SS	Briarcrest and Woodcrest	0.94	0.17±0.01	43±16	51±18	26±10
Range/SS	Old Ti Rd	0.93	0.24±0.02	89±25	118±35	35±13
Range/SS	Miramont	0.98	0.21±0.03	123±25	156±38	60±3
Wetland	Copperfield	0.97	0.37±0	367±61	586±99	103±20
Wetland	Austin Colony Park	0.95	0.29±0.01	148±25	211±33	51±11
Wetland	Lick Creek Park	0.88	0.34±0.01	239±20	362±34	71±4

APPENDIX F

CLUSTER ANALYSIS (10 CLUSTERS) OF DR-NIR SOURCE SPECTRA

Group		Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7	Cluster 8	Cluster 9	Cluster 10
1	Wilcox pasture soil	0	1	1	9	3	10	7	9	6	0
1	Lawyer dev low soil	0	1	1	9	3	10	7	9	6	0
1	Woodsman med dev soil	0	1	1	9	3	10	7	9	6	0
1	Briarcrest shrub scrub soil	0	1	1	9	3	10	11	9	6	8
2	N Country pasture soil	0	10	7	10	7	3	7	10	9	0
2	Marion Pugh dev low soil	0	10	7	10	7	3	7	10	9	0
2	Target high dev soil	0	10	7	10	7	3	7	10	9	0
3	Pigeon feces	1	4	3	1	10	4	6	0	7	10
3	Cow feces	1	4	3	1	10	4	6	0	7	10
3	Chicken feces	1	4	3	1	10	4	6	0	7	10
3	Chicken feces	1	4	3	1	10	4	6	0	7	10
3	Dog feces	1	4	3	1	10	4	6	0	7	10
4	Tap water	2	0	5	0	6	8	5	11	5	5
4	Tap water	2	0	5	0	6	8	5	11	5	5
4	Tap water	2	0	5	0	6	8	5	11	5	5
16	Cliff swallow feces	2	0	5	0	11	8	8	5	10	5
16	Cliff swallow feces	2	0	9	0	11	8	8	5	10	5
5	Effluent	2	11	9	0	11	8	8	5	10	5
5	Effluent	2	11	9	0	11	8	8	5	10	5
5	Effluent	2	11	9	0	11	8	8	5	10	5
5	Impervious runoff	2	11	9	0	11	8	8	5	10	5
5	Impervious runoff	2	11	9	0	11	8	8	5	10	5
5	Impervious runoff	2	11	9	0	11	8	8	5	10	5
5	Impervious runoff	2	11	9	5	11	8	8	5	10	5
5	Impervious runoff	2	11	9	5	11	8	8	5	10	5
6	Central Park dev open soil	3	2	11	2	0	5	0	2	3	4
6	Lick wetland soil	3	2	11	2	0	5	0	2	3	4

6	Miramont shrub scrub soil	3	2	11	2	0	5	0	2	3	4
6	Lick forest soil	3	3	7	2	7	5	0	2	3	4
6	Austin Col wetland soil	3	3	11	2	0	5	0	2	3	4
6	Azalea dev med soil	3	3	11	2	0	5	0	2	3	4
6	Briarcrest shrub scrub soil	3	3	11	2	0	5	0	2	3	4
6	Wilcox pasture soil	3	3	11	2	0	5	0	2	3	4
6	John Crompton forest soil	3	3	11	2	0	5	0	2	3	4
6	Old Ti Rd shrub scrub soil	3	3	11	2	0	5	0	2	3	4
6	Kathy Fleming forest soil	3	3	11	2	0	5	0	2	3	9
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
7	Effluent	4	6	6	6	1	7	1	7	2	6
8	Copperfield wetland soil	5	2	7	8	4	11	3	4	8	2
8	Wolf Pen dev open soil	5	2	10	2	0	1	0	2	3	4
8	Woodsman med dev soil	5	2	10	2	0	1	0	2	3	9
8	Haines dev low soil	5	2	10	8	4	11	0	4	8	2
8	Marion Pugh dev low soil	5	2	10	8	4	11	0	4	8	2
8	PO mall dev high soil	5	2	10	8	4	11	3	4	8	2
8	Austin Col dev open soil	5	2	10	8	4	11	3	4	8	2
8	Lawyer dev low soil	5	2	10	8	4	11	3	4	8	2
8	Target high dev soil	5	2	10	8	4	11	3	4	8	2
8	HEB high dev soil	5	2	10	8	4	11	3	4	8	2

8	Renaissance Park med dev soil	5	2	10	8	4	11	3	4	8	2
9	Engine oil	6	7	4	3	8	0	9	8	1	3
9	Engine oil	6	7	4	3	8	0	9	8	1	3
10	Wolf Pen dev open soil	7	10	7	10	4	3	3	10	9	2
10	Haines dev low soil	7	10	7	10	4	3	3	10	9	2
10	John Crompton forest soil	7	10	7	10	4	3	3	10	9	2
10	Lick wetland soil	7	10	7	10	4	3	3	10	9	2
10	Azalea dev med soil	7	10	7	10	7	3	3	10	9	2
10	Renaissance Park med dev soil	7	10	7	10	7	3	3	10	9	2
11	Lick forest soil	7	10	7	10	7	3	7	10	9	0
11	Austin Col wetland soil	7	10	7	10	7	3	7	10	9	0
11	Austin Col dev open soil	7	10	7	10	7	3	7	10	9	0
11	Kathy Fleming forest soil	7	10	7	10	7	3	7	10	9	0
11	Kathy Fleming pasture soil	7	10	7	10	7	3	7	10	9	0
11	N Country pasture soil	7	10	7	10	7	3	7	10	9	0
12	Impervious runoff	8	5	6	6	1	7	2	3	2	6
12	Impervious runoff	8	5	8	7	5	2	2	3	2	11
12	Impervious runoff	8	5	8	7	5	2	2	3	4	11
12	Impervious runoff	8	5	8	7	5	2	2	3	4	11
12	Impervious runoff	8	5	8	7	5	2	2	3	4	11
12	Impervious runoff	8	5	8	7	5	2	2	3	4	11
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7

13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Blank	9	8	0	4	9	6	4	1	0	7
13	Sponge	9	8	0	4	9	6	4	1	0	7
13	Sponge	9	8	0	4	9	6	4	1	0	7
13	Sponge	9	8	0	4	9	6	4	1	0	7
14	Human decomposition remains	10	9	2	11	2	9	10	6	11	1
15	Copperfield wetland soil	11	1	1	9	3	10	11	9	6	8
15	PO mall dev high soil	11	1	1	9	3	10	11	9	6	8
15	Central Park dev open soil	11	1	1	9	3	10	11	9	6	8
15	HEB high dev soil	11	1	1	9	3	10	11	9	6	8
15	Old Ti Rd shrub scrub soil	11	1	1	9	3	10	11	9	6	8
15	Miramont shrub scrub soil	11	1	1	9	3	10	11	9	6	8

APPENDIX G

PRECIPITATION DURING THE SAMPLING PERIOD. BOLD INDICATES SAMPLING DATE. ND INDICATES NO DATA.

Date	Precipitation KCLL mm	Precipitation KTXBRYAN10 mm
3/1/2011	0	0
3/2/2011	0	0
3/3/2011	0	0
3/4/2011	0	0
3/5/2011	9.7	0.5
3/6/2011	0	0
3/7/2011	0	0
3/8/2011	2.8	1.3
3/9/2011	0	0
3/10/2011	0	0
3/11/2011	0	0
3/12/2011	0	0
3/13/2011	0	0
3/14/2011	4.8	13.2
3/15/2011	0	0
3/16/2011	0	0
3/17/2011	0	0
3/18/2011	0	0
3/19/2011	0	0
3/20/2011	0	0
3/21/2011	0	0
3/22/2011	0	0
3/23/2011	0	0
3/24/2011	0	0
3/25/2011	0	0
3/26/2011	0	0
3/27/2011	0	0
3/28/2011	0	0
3/29/2011	0.3	0
3/30/2011	0	0
3/31/2011	0	0

4/1/2011	0	0
4/2/2011	0	0
4/3/2011	0	0
4/4/2011	0	2.0
4/5/2011	0	0
4/6/2011	0	0
4/7/2011	0	0
4/8/2011	0	0
4/9/2011	0	0
4/10/2011	0	0
4/11/2011	0	0
4/12/2011	0	0
4/13/2011	0	0
4/14/2011	0	0
4/15/2011	0	0
4/16/2011	0	0
4/17/2011	0	0
4/18/2011	0	0
4/19/2011	0	0
4/20/2011	0	0
4/21/2011	0	0
4/22/2011	0	0
4/23/2011	0	0
4/24/2011	0	0
4/25/2011	0	0.3
4/26/2011	0	0.3
4/27/2011	0	0
4/28/2011	0	0
4/29/2011	0	0
4/30/2011	0	0
5/1/2011	0	0
5/2/2011	1.0	1.3
5/3/2011	0	0
5/4/2011	0	0
5/5/2011	0	0
5/6/2011	0	0
5/7/2011	0	0
5/8/2011	0	0
5/9/2011	0	0
5/10/2011	0	0

5/11/2011	5.6	0.3
5/12/2011	42.2	17.8
5/13/2011	0	0
5/14/2011	0	0
5/15/2011	0	0
5/16/2011	0	0
5/17/2011	0	0
5/18/2011	0	0
5/19/2011	0	0
5/20/2011	22.6	30.0
5/21/2011	6.1	0.3
5/22/2011	0	0
5/23/2011	0	0
5/24/2011	0	0
5/25/2011	0	0
5/26/2011	0	0
5/27/2011	0	0
5/28/2011	0	0
5/29/2011	0	0
5/30/2011	0	0
5/31/2011	0	0
6/1/2011	0	0
6/2/2011	0	0
6/3/2011	0	0
6/4/2011	0	0
6/5/2011	0.5	0.8
6/6/2011	5.3	1.5
6/7/2011	0	0
6/8/2011	0	0
6/9/2011	0	0
6/10/2011	0	0
6/11/2011	0	0
6/12/2011	0	0
6/13/2011	0	0
6/14/2011	0	0
6/15/2011	0	0
6/16/2011	0	0
6/17/2011	0	0
6/18/2011	0	0
6/19/2011	0	0

6/20/2011	0	0
6/21/2011	0	0.5
6/22/2011	62.3	43.0
6/23/2011	0	0
6/24/2011	0	0
6/25/2011	0	0
6/26/2011	0	nd
6/27/2011	0	nd
6/28/2011	0	nd
6/29/2011	0	nd
6/30/2011	0	nd
7/1/2011	0	nd
7/2/2011	0	nd
7/3/2011	0	nd
7/4/2011	0	nd
7/5/2011	0	nd
7/6/2011	0	nd
7/7/2011	0	nd
7/8/2011	0	nd
7/9/2011	0	nd
7/10/2011	0	nd
7/11/2011	0	nd
7/12/2011	0	nd
7/13/2011	0	nd
7/14/2011	0	nd
7/15/2011	1.8	0.3
7/16/2011	0.8	0
7/17/2011	0	0
7/18/2011	0	1.8
7/19/2011	0	0
7/20/2011	0	0
7/21/2011	0	0
7/22/2011	0	0
7/23/2011	0	0
7/24/2011	0	0
7/25/2011	0	0
7/26/2011	0	0
7/27/2011	0	0
7/28/2011	0	0
7/29/2011	0	0

7/30/2011	0	0
7/31/2011	0	0
8/1/2011	0	0
8/2/2011	0	0
8/3/2011	0	0
8/4/2011	0	0
8/5/2011	0	0
8/6/2011	0	0
8/7/2011	0	0
8/8/2011	0	0
8/9/2011	0	0
8/10/2011	0	0
8/11/2011	0	0
8/12/2011	0	0
8/13/2011	0	8.4
8/14/2011	0	0
8/15/2011	0	0
8/16/2011	0	0
8/17/2011	0	0
8/18/2011	0	0
8/19/2011	0	0
8/20/2011	0	0
8/21/2011	0	0
8/22/2011	0	0
8/23/2011	0	0
8/24/2011	2.5	3.3
8/25/2011	3.3	2.0
8/26/2011	0	0
8/27/2011	0	0
8/28/2011	0	0
8/29/2011	0	0
8/30/2011	0	0
8/31/2011	0	0
9/1/2011	0	0
9/2/2011	0	0
9/3/2011	0	0
9/4/2011	0	0
9/5/2011	0	0
9/6/2011	0	0
9/7/2011	0	0

9/8/2011	0	0
9/9/2011	0	0
9/10/2011	0	0
9/11/2011	0	0
9/12/2011	0	0
9/13/2011	0	0
9/14/2011	0	0
9/15/2011	6.9	1.0
9/16/2011	0	0
9/17/2011	0.3	0
9/18/2011	0	1.8
9/19/2011	35.6	47.1
9/20/2011	0	0
9/21/2011	0	0
9/22/2011	0	0
9/23/2011	0	0
9/24/2011	0	0
9/25/2011	0	0
9/26/2011	14.5	0
9/27/2011	0	0
9/28/2011	0	0
9/29/2011	0	0
9/30/2011	0	0
10/1/2011	0	0
10/2/2011	0	0
10/3/2011	0	0
10/4/2011	0	0
10/5/2011	0	0
10/6/2011	0	0
10/7/2011	0	0
10/8/2011	0	0
10/9/2011	20.9	13.5
10/10/2011	0	0
10/11/2011	0	0
10/12/2011	1.3	0.3
10/13/2011	0.3	0
10/14/2011	0	0
10/15/2011	0	0
10/16/2011	0	0
10/17/2011	0	0

10/18/2011	0	0
10/19/2011	0	0
10/20/2011	0	0
10/21/2011	0	0
10/22/2011	0	0
10/23/2011	0	0
10/24/2011	0	0
10/25/2011	0	0
10/26/2011	0	0
10/27/2011	2.0	0.3
10/28/2011	0	0
10/29/2011	0	0
10/30/2011	0	0
10/31/2011	0	0
11/1/2011	0	0
11/2/2011	0	0
11/3/2011	0.3	0
11/4/2011	0	0
11/5/2011	0	0
11/6/2011	0	0
11/7/2011	0	0
11/8/2011	0.3	0
11/9/2011	0	0
11/10/2011	0	0
11/11/2011	0	0
11/12/2011	0	0
11/13/2011	0	0
11/14/2011	0	0
11/15/2011	7.4	31.0
11/16/2011	0	0.3
11/17/2011	0	0
11/18/2011	0	0
11/19/2011	0	0
11/20/2011	0	0
11/21/2011	3.1	1.8
11/22/2011	29.0	28.2
11/23/2011	0	0.3
11/24/2011	0	0.3
11/25/2011	0	0.3
11/26/2011	21.6	15.0

11/27/2011	0	0
11/28/2011	0	0
11/29/2011	0	0
11/30/2011	0	0
12/1/2011	0	0
12/2/2011	0	0
12/3/2011	0	0
12/4/2011	9.2	22.6
12/5/2011	2.3	3.1
12/6/2011	0	0
12/7/2011	0	0
12/8/2011	0	0
12/9/2011	0	0
12/10/2011	0	0
12/11/2011	0	0
12/12/2011	0	0
12/13/2011	0	0
12/14/2011	0.5	1.3
12/15/2011	3.6	5.1
12/16/2011	13.5	7.4
12/17/2011	0	3.3
12/18/2011	0	0
12/19/2011	3.1	8.6
12/20/2011	1.5	0.5
12/21/2011	1.8	4.8
12/22/2011	28.7	24.2
12/23/2011	0	0
12/24/2011	21.6	13.5
12/25/2011	0.3	0.5
12/26/2011	1.3	0.51
12/27/2011	0	0.3
12/28/2011	0	0
12/29/2011	0	0
12/30/2011	0	0
12/31/2011	0	0.3
1/1/2012	0	0
1/2/2012	0	0
1/3/2012	0	0
1/4/2012	0	0
1/5/2012	0	0

1/6/2012	0	0
1/7/2012	0	0
1/8/2012	1.8	4.1
1/9/2012	10.7	37.4
1/10/2012	0.3	0.3
1/11/2012	0	0
1/12/2012	0	0
1/13/2012	0	0
1/14/2012	0	0
1/15/2012	0	0
1/16/2012	0	0
1/17/2012	0.8	1.3
1/18/2012	0	0
1/19/2012	0	0
1/20/2012	0	0
1/21/2012	0	0
1/22/2012	0	0
1/23/2012	0	0
1/24/2012	20.6	16.0
1/25/2012	33.8	28.7
1/26/2012	0	0
1/27/2012	0	0
1/28/2012	0	0
1/29/2012	0	0
1/30/2012	0.5	0.3
1/31/2012	2.3	3.1
2/1/2012	0.3	0.5
2/2/2012	4.1	5.1
2/3/2012	104.6	9.4
2/4/2012	55	33.6
2/5/2012	0.3	1.8
2/6/2012	0	0

APPENDIX H

RUNOFF CURVE NUMBERS FROM USDA TR-55

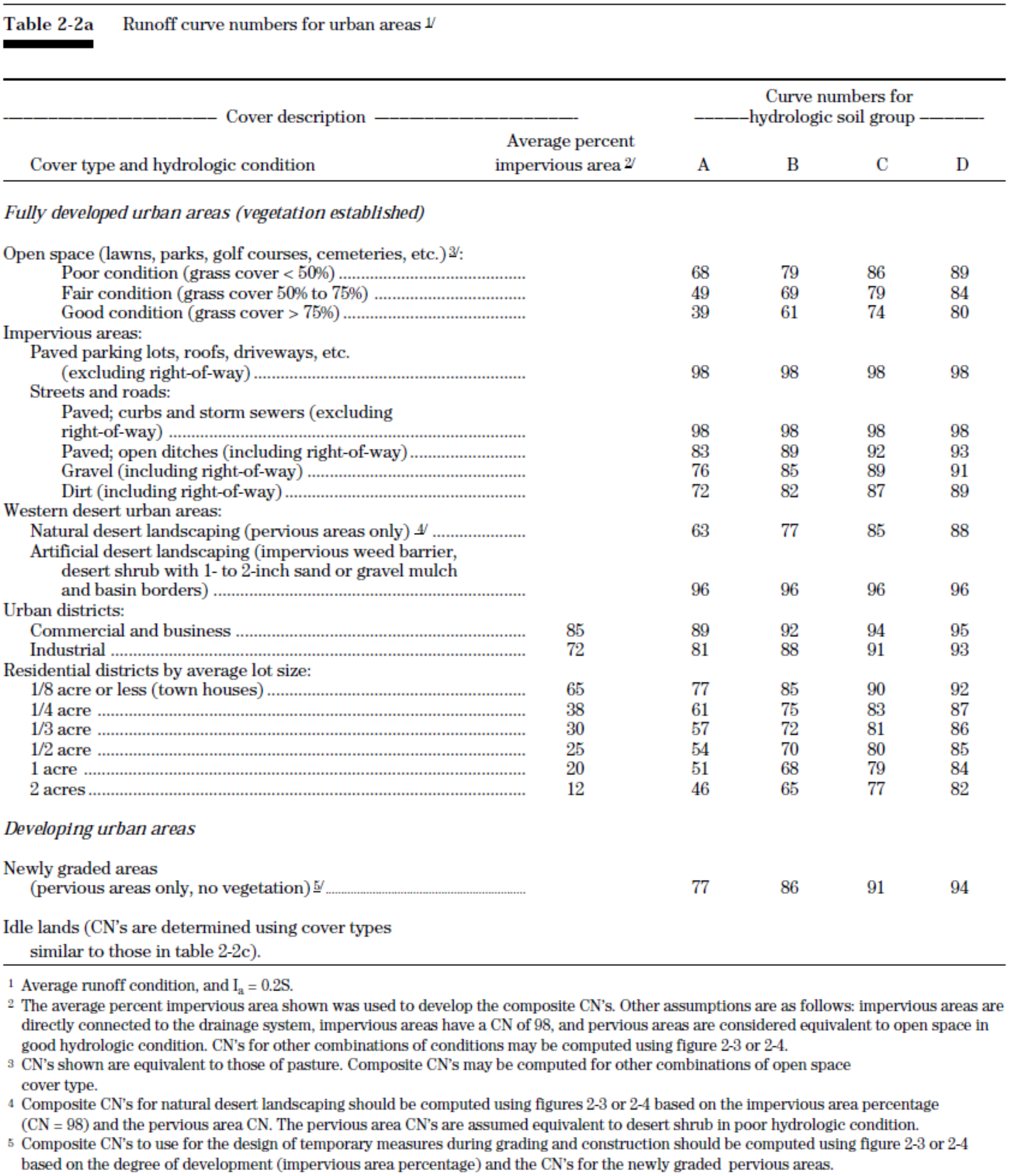


Table 2-2a Runoff curve numbers for urban areas [1]

Cover description		Curve numbers for hydrologic soil group			
Cover type and hydrologic condition	Average percent impervious area [2]	A	B	C	D
Fully developed urban areas (vegetation established)					
Open space (lawns, parks, golf courses, cemeteries, etc.) [3]:					
Poor condition (grass cover < 50%)		68	79	86	89
Fair condition (grass cover 50% to 75%)		49	69	79	84
Good condition (grass cover > 75%)		39	61	74	80
Impervious areas:					
Paved parking lots, roofs, driveways, etc. (excluding right-of-way)		98	98	98	98
Streets and roads:					
Paved; curbs and storm sewers (excluding right-of-way)		98	98	98	98
Paved; open ditches (including right-of-way)		83	89	92	93
Gravel (including right-of-way)		76	85	89	91
Dirt (including right-of-way)		72	82	87	89
Western desert urban areas:					
Natural desert landscaping (pervious areas only) [4]		63	77	85	88
Artificial desert landscaping (impervious weed barrier, desert shrub with 1- to 2-inch sand or gravel mulch and basin borders)		96	96	96	96
Urban districts:					
Commercial and business	85	89	92	94	95
Industrial	72	81	88	91	93
Residential districts by average lot size:					
1/8 acre or less (town houses)	65	77	85	90	92
1/4 acre	38	61	75	83	87
1/3 acre	30	57	72	81	86
1/2 acre	25	54	70	80	85
1 acre	20	51	68	79	84
2 acres	12	46	65	77	82
Developing urban areas					
Newly graded areas (pervious areas only, no vegetation) [5]		77	86	91	94
Idle lands (CN's are determined using cover types similar to those in table 2-2c).					

[1] Average runoff condition, and $I_a = 0.2S$.

[2] The average percent impervious area shown was used to develop the composite CN's. Other assumptions are as follows: impervious areas are directly connected to the drainage system, impervious areas have a CN of 98, and pervious areas are considered equivalent to open space in good hydrologic condition. CN's for other combinations of conditions may be computed using figure 2-3 or 2-4.

[3] CN's shown are equivalent to those of pasture. Composite CN's may be computed for other combinations of open space cover type.

[4] Composite CN's for natural desert landscaping should be computed using figures 2-3 or 2-4 based on the impervious area percentage (CN = 98) and the pervious area CN. The pervious area CN's are assumed equivalent to desert shrub in poor hydrologic condition.

[5] Composite CN's to use for the design of temporary measures during grading and construction should be computed using figure 2-3 or 2-4 based on the degree of development (impervious area percentage) and the CN's for the newly graded pervious areas.

Table 2-2b Runoff curve numbers for cultivated agricultural lands [1]

Cover description			Curve numbers for hydrologic soil group			
Cover type	Treatment [2]	Hydrologic condition [3]	A	B	C	D
Fallow	Bare soil	—	77	86	91	94
	Crop residue cover (CR)	Poor	76	85	90	93
		Good	74	83	88	90
Row crops	Straight row (SR)	Poor	72	81	88	91
		Good	67	78	85	89
	SR + CR	Poor	71	80	87	90
		Good	64	75	82	85
	Contoured (C)	Poor	70	79	84	88
		Good	65	75	82	86
	C + CR	Poor	69	78	83	87
		Good	64	74	81	85
	Contoured & terraced (C&T)	Poor	66	74	80	82
		Good	62	71	78	81
	C&T+ CR	Poor	65	73	79	81
		Good	61	70	77	80
Small grain	SR	Poor	65	76	84	88
		Good	63	75	83	87
	SR + CR	Poor	64	75	83	86
		Good	60	72	80	84
	C	Poor	63	74	82	85
		Good	61	73	81	84
	C + CR	Poor	62	73	81	84
		Good	60	72	80	83
	C&T	Poor	61	72	79	82
		Good	59	70	78	81
	C&T+ CR	Poor	60	71	78	81
		Good	58	69	77	80
Close-seeded or broadcast legumes or rotation meadow	SR	Poor	66	77	85	89
		Good	58	72	81	85
	C	Poor	64	75	83	85
		Good	55	69	78	83
	C&T	Poor	63	73	80	83
		Good	51	67	76	80

[1] Average runoff condition, and I_a=0.2S

[2] Crop residue cover applies only if residue is on at least 5% of the surface throughout the year.

[3] Hydraulic condition is based on combination factors that affect infiltration and runoff, including (a) density and canopy of vegetative areas, (b) amount of year-round cover, (c) amount of grass or close-seeded legumes, (d) percent of residue cover on the land surface (good ≥ 20%), and (e) degree of surface roughness.

Poor: Factors impair infiltration and tend to increase runoff.

Good: Factors encourage average and better than average infiltration and tend to decrease runoff.

Table 2-2c Runoff curve numbers for other agricultural lands [1]

Cover description		Curve numbers for hydrologic soil group			
Cover type	Hydrologic condition	A	B	C	D
Pasture, grassland, or range—continuous forage for grazing. [2]	Poor	68	79	86	89
	Fair	49	69	79	84
	Good	39	61	74	80
Meadow—continuous grass, protected from grazing and generally mowed for hay.	—	30	58	71	78
Brush—brush-weed-grass mixture with brush the major element. [3]	Poor	48	67	77	83
	Fair	35	56	70	77
	Good	30 [4]	48	65	73
Woods—grass combination (orchard or tree farm). [5]	Poor	57	73	82	86
	Fair	43	65	76	82
	Good	32	58	72	79
Woods. [6]	Poor	45	66	77	83
	Fair	36	60	73	79
	Good	30 [4]	55	70	77
Farmsteads—buildings, lanes, driveways, and surrounding lots.	—	59	74	82	86

[1] Average runoff condition, and $I_a = 0.2S$.

[2] *Poor:* <50%) ground cover or heavily grazed with no mulch.
Fair: 50 to 75% ground cover and not heavily grazed.
Good: > 75% ground cover and lightly or only occasionally grazed.

[3] *Poor:* <50% ground cover.
Fair: 50 to 75% ground cover.
Good: >75% ground cover.

[4] Actual curve number is less than 30; use CN = 30 for runoff computations.

[5] CN's shown were computed for areas with 50% woods and 50% grass (pasture) cover. Other combinations of conditions may be computed from the CN's for woods and pasture.

[6] *Poor:* Forest litter, small trees, and brush are destroyed by heavy grazing or regular burning.
Fair: Woods are grazed but not burned, and some forest litter covers the soil.
Good: Woods are protected from grazing, and litter and brush adequately cover the soil.

Table 2-2d Runoff curve numbers for arid and semiarid rangelands [1]

Cover description		Curve numbers for hydrologic soil group			
Cover type	Hydrologic condition [2]	A [3]	B	C	D
Herbaceous—mixture of grass, weeds, and low-growing brush, with brush the minor element.	Poor		80	87	93
	Fair		71	81	89
	Good		62	74	85
Oak-aspen—mountain brush mixture of oak brush, aspen, mountain mahogany, bitter brush, maple, and other brush.	Poor		66	74	79
	Fair		48	57	63
	Good		30	41	48
Pinyon-juniper—pinyon, juniper, or both; grass understory.	Poor		75	85	89
	Fair		58	73	80
	Good		41	61	71
Sagebrush with grass understory.	Poor		67	80	85
	Fair		51	63	70
	Good		35	47	55
Desert shrub—major plants include saltbush, greasewood, creosotebush, blackbrush, bursage, palo verde, mesquite, and cactus.	Poor	63	77	85	88
	Fair	55	72	81	86
	Good	49	68	79	84

[1] Average runoff condition, and I_a, = 0.2S. For range in humid regions, use table 2-2c.

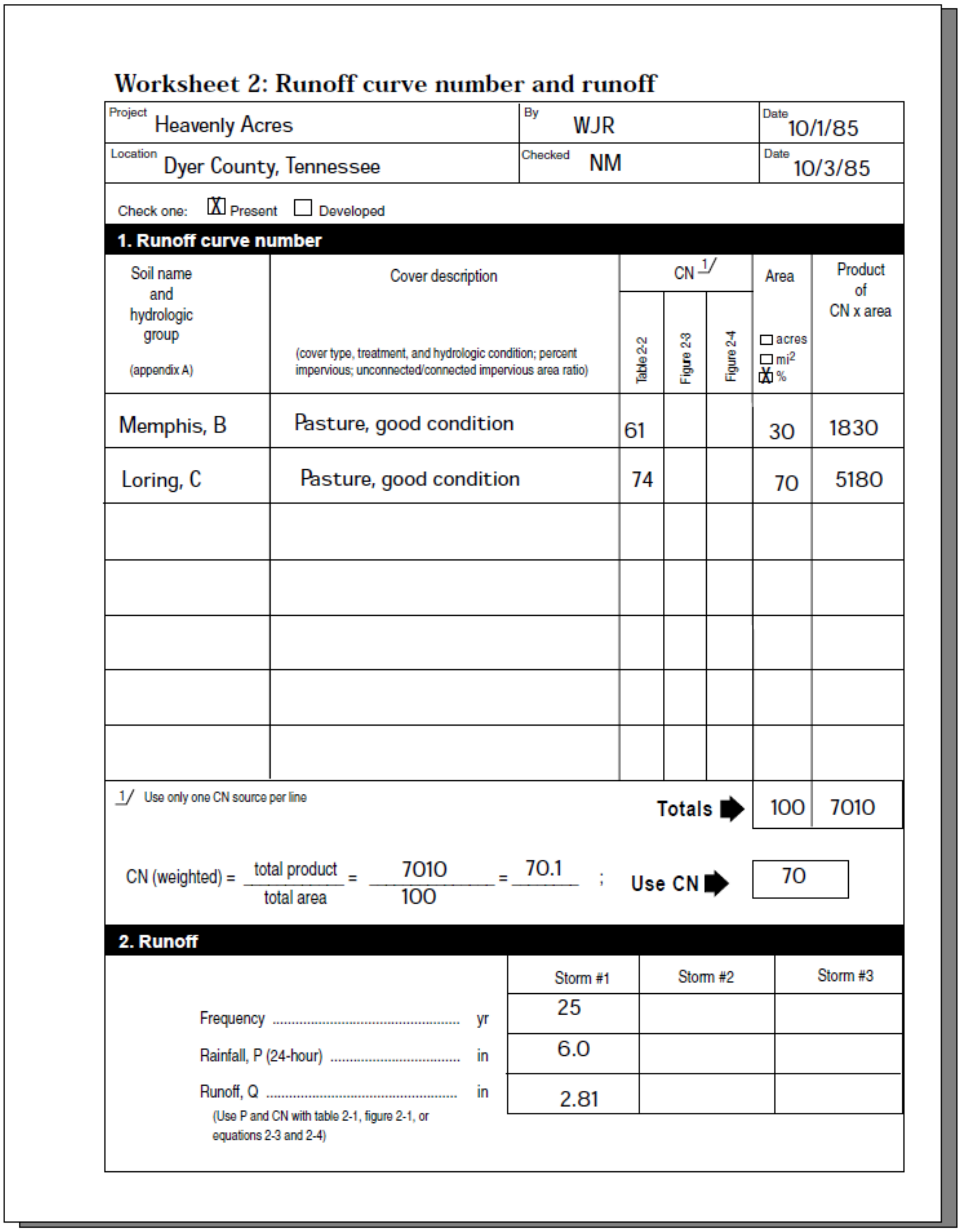
[2] Poor: <30% ground cover (litter, grass, and brush overstory).
Fair: 30 to 70% ground cover.
Good: > 70% ground cover.

[3] Curve numbers for group A have been developed only for desert shrub.

APPENDIX I

RUNOFF CURVE NUMBER WORKSHEET FROM USDA TR-55

Figure 2-5 Worksheet 2 for example 2-1



Worksheet 2: Runoff curve number and runoff

Project Heavenly Acres	By WJR	Date 10/1/85
Location Dyer County, Tennessee	Checked NM	Date 10/3/85

Check one: ☒ Present ☐ Developed

1. Runoff curve number

Soil name and hydrologic group (appendix A)	Cover description (cover type, treatment, and hydrologic condition; percent impervious; unconnected/connected impervious area ratio)	CN 1/			Area ☐ acres ☐ mi^2 ☒ %	Product of CN x area
		Table 2-2	Figure 2-3	Figure 2-4		
Memphis, B	Pasture, good condition	61			30	1830
Loring, C	Pasture, good condition	74			70	5180
1/ Use only one CN source per line				**Totals** ➡	100	7010

$$\text{CN (weighted)} = \frac{\text{total product}}{\text{total area}} = \frac{7010}{100} = 70.1$$

; **Use CN** ➡ 70

2. Runoff

		Storm #1	Storm #2	Storm #3
Frequency	yr	25		
Rainfall, P (24-hour)	in	6.0		
Runoff, Q (Use P and CN with table 2-1, figure 2-1, or equations 2-3 and 2-4)	in	2.81		