SURFACE WATER CHEMISTRY IN WHITE OAK CREEK, NORTH-EAST TEXAS: EFFECT OF LAND USE

A Thesis

by

ELIZA WATSON

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

December 2011

Major Subject: Water Management and Hydrological Science

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Approved by:

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ABSTRACT

Surface Water Chemistry in White Oak Creek, North-East Texas: Effect of Land Use.

(December 2011)

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Chair of Advisory Committee: Dr. Jacqueline A. Aitkenhead-Peterson

Over the last few decades increasing attention has been paid to the effects of land use activities and land management on stream water quality. Recent research has largely focused on dominant land uses such as urban development and agricultural cropland. The relative effect of land use activities and management on stream chemistry in sub-tropical rangeland ecosystems, where much of the land use is converted to pasture and agriculture is largely unknown. This study examined stream water quality and land use in a sub-tropical watershed in Northeast Texas largely dominated by rangeland. The study site, White Oak Creek Watershed located in the Sulphur River Basin, has been identified as an impaired stream due to low dissolved oxygen concentrations and subsequently listed on the Texas Commission for Environmental Quality's 303d list (TCEQ). In an attempt to determine potential sources of the low dissolved oxygen concentrations, twenty different chemical constituents were analyzed at 18 different sample sites in the tributaries of White Oak Creek and also along the main stem from April 2010 to March 2011. Dissolved oxygen concentrations over the study period were consistently above the minimum standard required by TCEQ and showed no indication

of impairment. Correlation analysis did not show any clear correlation between dissolved oxygen and any specific land use, or any chemical constituent. Some nutrients and suspended sediment concentrations were significantly different among the sub-catchments of White Oak Creek. Urban land uses were significantly and positively correlated to electrical conductivity, ammonium-N, magnesium, calcium, and dissolved organic carbon. Agricultural land use was significantly and positively correlated to orthophosphate-P, dissolved organic nitrogen, total suspended solids, and turbidity. Forests were inversely and significantly related to nitrate-N, orthophosphate-P, sulfate, dissolved organic carbon, total suspended solids, and turbidity. The study suggested that by maintaining a relatively high proportion of forested land in a watershed that water quality can be improved.

DEDICATION

To my family and loved ones for their endless support.

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1. INTRODUCTION

Rural watersheds are becoming increasingly threatened by diffuse sources of pollution and degraded water quality in much the same way that urban watersheds have. While much attention has recently focused on urban watersheds because of population density, point source pollutants, and runoff from impervious services, rural watersheds have been relatively neglected yet they face similar challenges as a result of nonpoint source pollution from activities such as extraction of natural resources, compromised septic systems, and agricultural practices. This thesis sought to understand the extent of the impacts to rural watersheds, specifically focusing on a rural northeastern Texas watershed. By examining linkages between rural stream water chemistry and land uses, the potential threats to a rural watershed's stream chemistry can be identified for watershed management and adoption of best management practices (BMPs).

1.1 Sediment Transport to Streams

Sedimentation of streams and its adverse affect on water quality is a result of both anthropogenic and natural causes resulting from increased watershed runoff and stream bank erosion and consequently leading to higher sediment loads. Problems associated with high sediment concentrations and loading include increased turbidity and higher nutrient loads leading to low dissolved oxygen concentrations, habitat destruction for benthic organisms, reduced habitat for fish spawning, and overall trophic disruptions

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This thesis follows the style of *Environmental Monitoring and Assessment.*

(Nelson and Booth 2002; Zimmerman et al. 2003). It is commonly observed and reported that the effect of one conditional characteristic from sediment transport and sedimentation leads to additional associated problems, as is the case with both turbidity and dissolved oxygen concentrations.

The two largest direct contributors of sediment to the stream system are through 1) erosion processes and failing stream banks associated with watershed land use, and 2) runoff or overland flow occurring after intense rainfall events. These two processes transport material into streams that can come in primarily two forms: as solid material or a solute. Each of these two forms can contain organic or inorganic components. The solid load can be further divided into bedload and suspended load. The type of load is largely dependent upon the relationship between flow conditions and the structure, density and size of the material (Owens et al. 2005). The suspended load is usually comprised of finer or less dense materials. In many stream systems, much of the suspended sediment is <2mm (sand size or less), with the large proportion of this being <63μm (silt and clay size). The <63μm size, fine-grained sediment, is an important fraction of the sediment within stream systems as it is the most chemically active component of the solid load due to its greater specific surface area and can therefore contain and transport both contaminants and nutrients (Owens et al. 2005). This fine-grained sediment load is generally cohesive and transported in the streams as aggregated particles. While bedload and coarse-grained sediment does not contribute to major water chemistry concerns, it can cause channel aggradations, reducing flow capacity that can

lead to flooding, navigational problems, and channel instability (Nelson and Booth 2002).

One critical impact of sediment influx to streams is the increase in turbidity. A study conducted by the California Department of Fish and Game highlighted the effects of stream bank erosion on turbidity and the productivity of the affected streams (Cordone and Kelley 1961). The department noted that increased turbidity from erosion led to an overall reduction in light penetration into the water, thereby limiting the growth of phytoplankton and other aquatic plants by disrupting photosynthetic processes. Both plants and phytoplankton play a critical role in the basic food chain for aquatic animals, and also as producers of oxygen. The limited photosynthetic processes are disruptive to natural stream re-aeration and purification processes, which involve the functioning of aquatic plants and plankton (Cordone and Kelley 1961). Increased turbidity from erosion and sedimentation affects aquatic animals through reducing the feeding efficiency of visual predators and filter feeders, again disrupting the natural food chain in streams. Sediments can also cause physical damage to aquatic invertebrates by clogging their gill surfaces and lowering their respiratory capacity (Department of Natural Resources, Wisconsin 2005).

Land use activities have been linked to increased concentrations and loads of sediments and the associated negative impacts of such in our surface waters. Research conducted on sediment transport to the Issaquah creek watershed in Washington state concluded that sediment transported to channels from urban areas, construction sites, agriculture areas, and road-surface erosion can reach the channel network only by

transport in suspension and therefore are largely fine-grained in particle size. On the other hand, bank erosion and landslides contributed to the mixed sediment fractions with particle sizes both ‘fine’ and ‘coarse’ grained (Nelson and Booth 2002). Other land use studies have been conducted on the effects of agricultural practices and their implication for stream sediment loads. For example, a study was completed in Pennsylvania on 29 impaired and unimpaired streams using sediment as the indicator factor. The researchers compared forested land cover with agriculture land and showed that nutrient and sediment concentrations and loads were positively correlated with the magnitude of development and agricultural practices within the watersheds. Forested land cover in their watersheds exported very low loads of pollutants in comparison with loads from agricultural land cover (Sheeder and Evans 2004).

Livestock grazing in riparian zones has been shown to increase the potential for stream sediment transport and associated effects on water quality. Stream and riparian ecosystems were studied in the western United States to understand the influence of cattle grazing on riparian habitats. The study concluded that significant disturbances from cattle in riparian zones lead to greater erosion and soil loss into streams, increasing bacteria and nutrients in stream channels from their adsorption to soil particles, and increases in runoff due to loss of infiltration capacity as a result of compaction (Belsky et al. 1999).

1.2 Nitrogen

Understanding the pathways in which inorganic forms of nitrogen are transported to watersheds is crucial for the evaluation and amelioration of land management practices to improve aquatic ecosystem health. Excess nitrogen concentrations in surface waters have been linked to eutrophication of coastal waters such as the Chesapeake Bay and the Gulf of Mexico (Goolsby et al. 2001; Shields et al. 2010; Brush 2009). The nitrification process in soils is critical to understanding the mobility of nitrate. Ammonium ions, a common fertilizer contribution, are transformed to nitrite and nitrate ions through oxidation by nitrifying bacteria. Transformation from a positively charged ion, which can be bound by negatively charged clay particles, to a negatively charged ion, allows for greater mobility in soil water (Atlas and Bartha 1987). Nitrate in the soil is readily available and utilized by plants; however this form of nitrogen can also be readily leached from the soil matrix into groundwater or flushed from watershed soil as through flow or Hortonion overland flow to surface waters during rain events. Research conducted in undisturbed forest watersheds has also revealed that riparian zones can serve as a source of nitrate due to the flushing effect of subsurface storage during rainstorms and snowmelts (Ranalli and Macalady 2010; Poor and McDonnell 2006). Many studies have shown that a large proportion of the nitrate found in agricultural streams is associated with baseflow (Wagner et al. 2008; Poor and McDonnell 2006; Daniel et al. 2009) and this is likely due to long term fertilization with nitrate reaching the groundwater table. A study in Eagle Creek Watershed in Central Indiana on an agricultural watershed and a mixed land use watershed showed differences

in nitrate flowpaths between the two watersheds. The agricultural watershed pre-storm event median nitrate concentration at baseflow was 5.9 mg/L while the pre-storm event median nitrate concentration for the mixed land use watershed was 0.7 mg/L. Following three storm events, mean concentrations for the agricultural watershed were 3.90 mg/L, 6.22 mg/L, and 4.40 mg/L with nitrate concentrations consistently peaking on the rising limb of the hydrograph. While the mixed land use watershed had mean nitrate concentrations of 0.55 mg/L, 1.52 mg/L, and 1.21 mg/L with nitrate concentrations consistently peaking on the falling limb of the hydrograph. This data suggests that an overall dilution effect is occurring on the existing nitrate concentrations in the baseflow of the agriculture watershed, while in contrast, a contribution of nitrate from upper soil horizons is occurring from the mixed land use watershed (Wagner et al. 2008).

Seasonal trends in an agricultural catchment were apparent in a study by Poor and McDonnell (2006) on three sub-catchments of the Oak Creek Watershed in Oregon. The sub-catchments: forested, agricultural, and residential showed varied nitrate concentration data in each of the catchments. The nitrate concentrations in the forested catchment were consistently low through all seasons while the agricultural catchment displayed seasonal variation with concentrations high in fall after fertilizer application, and subsequent dilution to medium concentrations in winter, and low in spring and a dry streambed during the summer months. Nitrate concentrations were consistently high in the residential catchment and were accredited to high flow rates with a constant source of nitrate (Poor and McDonnell 2006).

Isotopic composition of nitrate has emerged as a tool to identify sources of nitrate in a watershed. Barnes and Raymond (2010) studied seasonality and nitrate sources in fifteen headwater catchments within the Farmington River, Hockanum River, and Broad Brook Watersheds in Connecticut and Massachusetts using isotopic composition of nitrate. The watersheds, draining agriculture, urban, and forested land, had mean NO_3^--N concentrations of 3.47 mg/L, 1.93 mg/L, and 0.01 mg/L, respectively. Agricultural watersheds had the highest nitrate-N concentrations, as well as exhibiting seasonal variations with higher NO_3-N concentrations in August, and lowest in October. Studying the isotopic composition of the nitrate for each of the land uses revealed different sources. Agricultural sites had higher N enriched sites, consistent with the type of sources from manure waste. Urban streams signified a varying degree of N sources, implying that no one nitrogen source dominated, which the researchers determined was typical of septic waste. Forested watersheds did not contain the isotopic composition of dominant anthropogenic nitrogen sources to the system (Barnes and Raymond 2010).

1.3 Phosphorus

Phosphorus is another necessary nutrient for plant growth in both terrestrial and aquatic ecosystems. The over-application of phosphorus can however lead to negative water quality impacts, and possibly eutrophication, if excess phosphorus is transported into surface waters and it is the limiting nutrient. Eutrophication restricts water use activities and can be fatal to aquatic life due to the excessive growth of algae and aquatic weeds that occur with accumulation of agricultural run-off to surface waters. The

decomposition of excess aquatic plant growth creates a hypoxic environment that is unsuitable for native aquatic life. Phosphorus concentrations that can cause eutrophication typically range from 0.01 to 0.03 mg/L (Sharpley et al. 1996). Sharpley et al. (2001) concluded through ongoing research that most P exported from agricultural watersheds originates from only a small portion of the landscape where the concentrations of soil-P are very high. These 'critical source areas' are vulnerable to P loss via surface runoff and are dependent on contributing transport characteristics of the landscape as well as site management factors. Critical transport factors have been identified as erosion, surface runoff, subsurface flow, and connectivity of the site to the stream channel. Site management factors that influence P export to surface waters include high soil test P concentrations, and the rate, type and method of P application.

A study conducted by Ballantine et al. (2009) indicated that different land uses affected the P content of deposited sediment in streams in two lowland agricultural catchments in Dorset, U.K. One of the catchments was >80% pasture land, while the other was >80% cereal cultivation. Their results showed that greater P enrichment of the soils in surface runoff came from the cultivated land, even though total P content was greater in the pasture source soils than the cultivated source soils. Furthermore when they examined sediment in surface runoff it showed a greater degree of finer particles associated with sediment in runoff transported from cultivated land. Ballantine et al. (2009) concluded that regular and intensive application of fertilizers on cultivated land contributed to the higher P content in these soils, while higher organic matter content in

the pasture soils allowed for greater incorporation and retention in soils, and hence less mobility.

Banner et al. (2009) showed that in twenty-five Kansas streams large exports of phosphorus occur during high-discharge events. Their research showed that an average of 88% of the total annual P load occurred during flows that occur only 10% of the time. Overall, median concentrations for total phosphorus ranged from 0.05 mg/L to 0.33 mg/L with the greatest median concentrations occurring in the spring, and the lowest in winter. Furthermore their study indicated that the percentage of cropland alongside the streams which were within riparian zones, were generally the strongest predictor across seasons of median total P concentrations.

1.4 Cations

Increased concentrations of major base cations (sodium, potassium, calcium, magnesium) have been recorded from a large array of activities. A study conducted in the Muskegon River Watershed in Michigan compared land uses with export of major ions to streams. They concluded, that all the major cations were observed to be higher in surface waters draining watersheds having a large proportion of urban and agricultural land uses relative to watersheds with a large proportion of forests. Urban watersheds had higher concentrations of Na^+ and K^+ than agricultural watersheds, while agricultural watersheds had higher Ca^{2+} and Mg^{2+} than urban watersheds (Ray et al. 2010). High potassium concentrations were most strongly associated with urban and agricultural land uses in a Massachusetts watershed (Dow et al. 2006; Williams et al. 2005). Increased

cation concentrations have been consistently observed in urban streams across the United States (Paul and Meyer 2001; McConnell 1980; Smart et al. 1985). A recent study suggested that increased carbonic acid (H_2CO_3) as a result of increased atmospheric CO_2 is likely responsible for release of soil cations in deforested tropical ecosystems (Markewitz et al. 2006) and a similar occurrence may be responsible for losses of calcium and magnesium in agricultural and potassium in urban soils.

Chen and Driscoll (2009) conducted a study on twenty-two river sites along the New York coast of Lake Ontario. They observed that major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) tended to exhibit seasonal patterns in streams, with concentrations generally lowest during the spring period (March-May). Cation concentrations then increased in late summer/early fall and decreased as discharge increased during late fall and early winter. Additionally, the study showed that higher cation concentrations were observed at sites with greater agricultural land cover which was contributed to factors such as fertilizer and manure applications, enhanced mineralization of organic matter, and weathering (Ahearn et al. 2004; Chen and Driscoll 2009).

Weathering of bedrock geology contributes cations to stream water. In a study located in southwest Germany, geology explained the highest percentage of total variance when determining sources of Ca^{2+} and Mg^{2+} ions (Xie et al. 2005). Geologic formations made up of easily soluble minerals of carbonate and evaporatic lithological origin were observed to be the main source of calcium and magnesium to the stream water. In countries with dominant carbonate geology, such as the United States, both Ca^{2+} and Mg^{2+} can be contributed through the two main minerals found in limestone:

calcite ($CaCO_3$) and dolomite ($CaMg[CO_3]_2$) as a result of weathering (Szramek et al. 2007).

Higher concentrations of sodium were also found in a study on all Texas aquifers in areas where the bedrock geology was primarily limestone, marine formations (Hudak 1999). Natural salt dissolution from these formations can contribute sodium ions into the groundwater. Additionally, in areas such as the southwest United States, heavy pumping for agricultural irrigation or oil and gas exploration contributes a number of chemical constituents, including sodium ions to the surface that can potentially be drained into adjacent watersheds (Hudak 1999).

1.5 Anions

The most common anions observed in surface waters include chloride, sulfate, and fluoride. Chloride concentrations were observed to be the strongest indicator of anthropogenic disturbance in streams in a study conducted across the Mid-Atlantic region (Herlihy et al. 1998; Dow et al., 2006). Chen and Driscoll (2009) further suggested that Cl^- concentrations were a valuable indicator of human disturbance and urbanization of a watershed. On the contrary, chloride as an indicator of agricultural activities did not prove to be useful (Chen and Driscoll 2009).

Sulfate has multiple sources and sinks due to its high reactivity. High concentrations of sulfate have the potential to contribute to soil salinity, limit plant water uptake, and negatively impact water quality (Scanlon et al. 2009). Sources of sulfate can be derived from atmospheric deposition which includes anthropogenic sources such as

industrial fallout in addition to land applied fertilizer, irrigation water, and also geological sources, mainly gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and pyrite (FeS_2) that are weathered in the watershed (Scanlon et al. 2009). Sulfate and chloride also show seasonality; decreasing with increased discharge in the fall and winter, and increasing at a return to baseflow in the spring and summer (Chen and Driscoll 2009) suggesting a predominant groundwater source. Sulfate and fluoride also exhibit a strong correlation with agricultural land cover (Chen and Driscoll 2009). Fluoride has been observed to be toxic at high concentrations. Concentrations of fluoride ranging from 0.1 to 2.5 mg/L found in groundwater in the Ganga Plain in India were severe enough to cause skeletal and dental fluorosis to humans consuming the water (Misra and Mishra 2007). Groundwater F concentrations in groundwater were even higher in Andhra Pradesh, India and concentrations of up to 5.65 mg/L were found (Arveti et al. 2011). Sources of fluoride include atmospheric deposition, as well as mineral weathering (from fluorite and apatite), pesticides, and impurities in fertilizers (Scanlon et al. 2009).

1.6 Dissolved Organic Carbon

Sources of dissolved organic carbon (DOC) can vary greatly depending upon watershed characteristics. In general, the primary sources of DOC are derived from organic soils, vegetation, and wastewater effluent (Aitkenhead-Peterson et al. 2003; Aitkenhead-Peterson et al. 2009). A study conducted on the River Swale in Yorkshire, U.K. showed that diffuse sources of soil organic carbon dominated in some catchments during high flow conditions, particularly in those catchments that contained a large

storage of organic carbon in the soil (Eatherall et al. 2000). Conversely, during periods of low flow, these same catchments were dominated by sewage point sources of DOC, unless very high carbon deposits were present in the soil (Eatherall et al. 2000). The Eatherall et al. (2000) study supported the findings by Aitkenhead et al. (1999) who suggested that the proportion of peat cover in a watershed was a reliable predictor of surface water DOC concentrations. The quantity and quality of allochthonous sources of DOC in streams are largely driven by the type of soil organic matter, character of hydrologic flowpaths, and amount of wetland area in a basin (Aitkenhead-Peterson et al. 2003; Johnson et al. 2009).

Research on the effect of land use on DOC export is highly variable. Eighteen headwater streams draining forested, agriculture, and urban land uses in southwest Michigan were studied and the researchers found no correlation between type of land use and dissolved organic carbon (Johnson et al. 2009). Research on Eagle Creek Watershed in Indiana also reported that precipitation characteristics and discharge act as the primary controls on stream DOC concentrations during storms and not land use when comparing an agricultural catchment and a mixed land use catchment (Wagner et al. 2008). On the other hand, research in Red Hill State Forest in Australia showed that stream waters in a forested catchment had higher DOC concentrations than those stream waters in a pasture catchment, on average 13.8 mg/L and 9.6 mg/L, respectively. This was attributed to greater input and subsequent breakdown of leaf-litter in the forest catchment (Vink et al. 2007). Piatek et al. (2009) indicated that sources of DOC during high discharge events of summer and fall come from near-surface soil water, and runoff from wetlands. Their

study showed that samples taken from streams draining wetlands exhibited higher DOC concentrations and some of the lowest NO_3^- concentrations. This observation is consistent with incomplete and slow organic matter breakdown in conditions of low oxygen wetlands. Aitkenhead-Peterson et al. (2005, 2007) suggested that to remove the variability of DOC export within watershed land cover or land use it was better to examine soil C:N ratio's which were a robust predictor of DOC export (Aitkenhead-Peterson and McDowell 2000).

More recently research on riverine DOC from urban watersheds has become available (Sickman et al. 2007; Aitkenhead-Peterson et al. 2009; Petrone 2010). Sources of DOC from the urban landscape have been postulated as sewage effluent and carbon loss from watershed soils due to irrigation of turfgrass with high pH, high sodium irrigation water.

1.7 Dissolved Oxygen

Dissolved Oxygen (DO) is a critical component of stream water quality and the concomitant ability of a stream to support its aquatic life. The combination of turbidity, additional nutrients, and substrate settling all contribute to low concentrations of dissolved oxygen in surface waters, largely as a result of increased sediment loads. The addition of nutrients stimulates bacterial action to break down the organic waste (Cordone and Kelly 1961). To do so, the bacteria that break down the nutrients require oxygen and contribute to the overall reduction of dissolved oxygen in streams (Cordone and Kelly1961). It is common for DO concentrations to fluctuate both seasonally (Crowe

and Bayer 2005), and diurnally (Miltner 2010) as a result of in-stream photosynthetic processes. Miltner (2010) studied 109 survey sites in Ohio in an effort to understand nutrient criteria thresholds for analysis of aquatic health and found that dissolved oxygen concentrations falling below the established water quality standard of 4.0 mg/L have the potential to negatively impact aquatic life. Additionally, wide swings in DO fluctuation (>4.0 mg/L) throughout the day appeared to be particularly detrimental to biological communities (Miltner 2010). A study by Berka et al., (2001) on the Sumas River Watershed located along the British Columbia/Washington State border, examined the impact of agricultural land use on dissolved oxygen concentrations. Their findings showed that agricultural intensification in the watershed, particularly as a result of heavy manure application in the fall resulted in decreased dissolved oxygen concentrations; exhibiting a significant negative relationship between surplus nitrogen application and DO (Berka et al. 2001).

Overall, it appears that any input to surface waters that will initiate microbial breakdown of organic substrate such as limiting nutrients will result in reduced DO concentrations.

1.8 Land Use: Effect on Nutrient Inputs to Watersheds

The impacts of land use and land management practices on stream water chemistry have been widely studied in an effort to understand and determine causes of impairment to surface waters. Numerous studies have shown that different land uses contribute differently to stream water chemistry. (e.g., Bolda and Meyers 1997; Poor and

McDonnell 2006; Vink et al. 2007; Wagner et al. 2008; Johnson et al. 2009; Scanlon et al. 2009; Molinero and Burke 2009; Steele and Aitkenhead-Peterson 2011; Petrone 2010).

1.8.1 Urban Development

It is widely recognized that urban development in watersheds and close to surface waters can significantly alter water quality. For example, increases in nearly all constituents have been documented with particular emphasis on the consistency of oxygen demand, conductivity, suspended sediments, ammonium, hydrocarbons, and metals (Paul and Meyer 2001).

The expansion of development and urban areas fueled by population growth ultimately leads to increases in impervious surfaces. Arnold and Gibbons (1996) studied the impacts of impervious surfaces on surface runoff as a mechanism for understanding contaminant pathways. Their research showed that as the proportion of impervious surface cover in a watershed increased to 10-20% from prior land cover, runoff increased from 10% to 20%; a 35-50% increase in a watersheds impervious surface resulted in a threefold increase in runoff to 30%; 75-100% impervious surface increase in a watershed resulted in 50% of the incoming precipitation being lost to runoff instead of the natural watershed soil infiltration.

In urban areas, studies have shown that a significant portion of sediment, up to 40%, is derived from sources such as solids from sewage treatment works and roads, often containing higher concentrations of contaminants and nutrients (Owens et al. 2005). The correlation between land use and sediment loads, although not unique to

sedimentation issues, is particularly important given that many nonpoint sources of pollution can be transported to streams through their adsorption to clays and metal oxyhydroxides and eroded as sediment particles.

Wastewater treatment plants (WWTP) contribute a unique composition of nutrients into surface waters by point source inputs. Point sources from a WWTP can add significant amounts of solutes, particularly nitrate, sulfate, phosphate, chloride, and sodium to streams (Lewis et al. 2007; Steele et al. 2010; Aitkenhead-Peterson et al. 2011; Steele and Aitkenhead-Peterson 2011), as well as the addition of dissolved organic carbon and nitrogen (Sickman et al. 2007; Aitkenhead-Peterson et al. 2009; Petrone 2010). Other studies have emphasized the impact of construction in developing areas on surface water quality (Carpenter et al. 1998; Line et al. 2002). Construction sites increase erosion rates of the watershed landscape contributing to sediment transport to streams. The eroded material contributes to siltation of water bodies as well as to eutrophication because orthophosphate, which binds tightly to mineral soil adsorption sites, is carried with the eroded sediment (Carpenter et al. 1998; Line et al. 2002). When compared to other land uses or landscape disturbances, construction sites tend to contribute to higher total suspended sediments (TSS) in surface waters due to runoff from exposed soils at these sites (Line et al. 2002). While sewage effluent and construction are commonly associated with areas of urban development, it does not exonerate them from impacts to surface waters in rural watersheds although perhaps on a smaller scale.

Faulty residential septic systems, more common in rural watersheds, can input a similar composition of solutes to those found in WWTP point source effluent into surface waters. Impervious surfaces such as roads and construction sites are also relevant impacts in rural watersheds. In addition rural watersheds contain land uses that are not typically found in urban catchments but will also negatively impact the chemistry of rural surface waters.

1.8.2 Agriculture

Two major sources of nutrient over-enrichment in streams from agricultural non-point-source (NPS) pollution are nitrogen and phosphorous (Carpenter et al. 1998). It is largely recognized that the greater the proportion of agriculture in a watershed, the greater nutrient inputs into surrounding surface waters are observed. Reimann et al. (2009), found elevated concentrations of nitrate ranging from 2 to 20 mg/L in low-lying agricultural areas outside of Oslo, Norway. Similar findings were observed in Eagle Creek Watershed, Indiana where nitrate concentrations were recorded to be significantly higher in an agricultural watershed (2.5 mg/L to 14.3 mg/L) relative to a mixed land use watershed (0.3 mg/L to 3.3 mg/L) (Wagner et al. 2008).

Approximately 31% of the nation's stream length (207,355 miles) has high concentrations of phosphorus, and 32% have high concentrations of nitrogen (USEPA 2007). Eutrophication is caused by excessive inputs of phosphorous and nitrogen to surface waters in watersheds with a high percentage of agriculture land, and accounts for approximately 6% of the impaired streams in the United States (Carpenter et al. 1998). Inputs of N and P in agricultural watersheds are generally derived from excess

fertilization and manure production (Carpenter et al. 1998). Agricultural fertilizer inputs of phosphorus, at concentrations greater than output, has created an imbalance that has increased soil phosphorus to concentrations of concern (Daniel et al. 1998). During heavy runoff events, the excess P bound to eroded soils and sediment can then be delivered to surface waters via surface or subsurface flows (Correll 1998). Similarly, a surplus of N, particularly nitrate, which has high mobility in many watersheds soils, leaches readily to surface waters.

Manure can contribute a significant amount of phosphorus loading into adjacent streams from livestock agriculture (James et al. 2007). Contributions from dairy cattle in a watershed in southeastern New York showed that in-stream fecal deposits from pastured cattle represented 10% of watershed phosphorus loadings (James et al. 2007). Additionally, it was found that livestock grazing along streams and riparian zones can also have adverse effects on surface water quality by increasing turbidity, water temperature, bacteria, and overall nutrient concentrations (Belsky et al. 1999). Another study showed that nitrate + nitrite, total Kjeldahl nitrogen, total phosphorus, and sediment loads were reduced by 33, 78, 76, and 82 percent, respectively, after BMPs were implemented using a livestock exclusion fence along a riparian corridor in North Carolina to reduce the influx of pollutants resulting from livestock access to streams (Line et al. 2002).

Low agricultural intensity watersheds tend to have lower concentrations of most phosphorous fractions than predominately arable watersheds (Jarvie et al. 2010). On the contrary, livestock farming has resulted in higher concentrations of P, DON, and DOC,

demonstrating that intensive cattle farming in close proximity to stream channels is a major source of organic and particulate N and P (Jarvie et al. 2010).

1.8.3 Forestry

Rural watersheds are impacted by industries other than agriculture. For example, timber harvesting within a watershed catchment can result in temporary watershed soil disturbances and water quality degradation in nearby streams due to different activities such as road building, harvesting, fire and timber salvage which are all involved in the harvesting process (Bolda and Meyers 1997). The harvesting of timber in watersheds with some forestry is capable of changing several aspects of a watershed through changes in plant water uptake and hence evapotranspiration (ET), hydrologic flow paths through changed volumes of water reaching the watershed soil and subsequently altering stream water sediment transport, nutrient concentrations, and overall biogeochemical cycling (Gravelle et al. 2009). Removal of vegetation, particularly in the riparian zone, during harvesting can also cause increases in stream water temperature, which will decrease oxygen solubility (Gravelle et al. 2009). A study conducted in the Pacific Northwest U.S. on a watershed before and after timber harvest observed a five-fold increase in nitrate concentrations in adjacent stream water following harvest (Gravelle et al. 2009). The study in the Pacific Northwest supported the earlier experiments conducted at Hubbard Brook Experimental Station in New Hampshire which showed similar results after clear-cutting. Increases in NO_3^-, Ca^{2+}, and K^+ in stream water chemistry were documented in the first three years following harvest at Hubbard Brook during their clear-cutting and strip-cutting timber harvests (Martin et al. 1984).

1.8.4 Mining

Surface mining has adverse affects on nearby watershed water quality if BMPs are not followed. Mining activity in a watershed is conducive to high sediment loads in streams and rivers. Stream chemical analysis of historic and ongoing mining activities on the Susquehanna River in Pennsylvania and New York revealed elevated acidity, turbidity, and sulfate concentrations in areas of intensive and intermediate mining (Bruns 2005). Yet, alkalinity and pH were recorded as being sufficiently high in surface waters therefore minimizing the risk of acid mine drainage in the study area (Bruns 2005). The Bruns (2005) study indicated that although acid mine drainage was not necessarily present, residual mine drainage could still impact water quality within the watershed. Further, when compared to areas of urbanization and agriculture in the study, it was concluded that impacts to streams by mining exceeded those impacts from the other land uses (Bruns 2005). Not all incidences of low pH and high sulfate and metal concentrations in surface waters are indicative of mining however. Weathering of black shales or pyrite containing rocks in a watershed, particularly those exposed by road cutting, can also be observed in stream chemistry, particularly in relation to sulfate concentrations (Tuttle et al. 2009).

The impact of mining activity around Lake Coeur d'Alene and the Coeur d'Alene and Spokane river basins in Idaho and Washington, USA was investigated by Owens et al. (2005). Prior to the establishment of mine tailings ponds in 1968, highly enriched mine tailings, were being directly discharged into local surface waters. Subsequent studies during the 1990s showed that 70×10^6 tons of trace-element rich

sediments had settled in Lake Coeur d'Alene with additional quantities of trace-element rich sediments entering into the river system. Estimates of the sediment chemical composition showed that 10% was composed of mine tailings with the remaining 90% composed of background sediment material. This hazardous sediment composition has extreme implications for the water quality of the affected rivers, the aquatic life, and downstream users.

1.9 Objectives of Study

The objectives of this study were to investigate land use and stream chemistry dynamics of a rural watershed in the Post Oak Savannah region of Northeast Texas. Persistent drought conditions in the South have necessitated the need for a greater and more expansive degree of monitoring of our surface waters for their future protection. Understanding how land use may jeopardize or impact the quality of our waters and finding ways to manage these effects are inherent to the purpose of this research. The research broadens the available data on US surface waters and nutrient concentrations and loads exported downstream to reservoirs for drinking water supply.

Specific objectives of this study were to: (1) quantify nutrient suspended sediment, dissolved oxygen and general stream chemistry within tributaries and the main stem of the White Oak Creek Watershed; and (2) identify and map land uses within the studied sub-watersheds using GIS software. And, examine relationships between existing land uses and stream chemistry.

1.10 Hypotheses

Objective 1: Quantify nutrient suspended sediment and dissolved oxygen concentrations within tributaries and the main stem of the White Oak Creek Watershed

1. H_0: Nutrient, suspended sediment and dissolved oxygen concentrations will not be significantly different in the sub-catchments sampled

2. H_1: There will be significant differences in water chemistry among the sub-catchments sampled

3. H_2: Nutrient and sediment concentrations are positively and significantly correlated to dissolved oxygen concentrations among White Oak Creek Watershed sub-catchments

1. Objective 2: Examine relationships between existing land uses and stream chemistry H_0: There is no relationship between any watershed land use and nutrient concentrations, sediment loads, and dissolved oxygen concentrations in White Oak Creek Watershed and its sub-catchments

2. H_1: There is a positive and significant correlation between nutrient concentrations in White Oak Creek sub-catchments and land use

2. MATERIALS AND METHODS

2.1 Site Description

The White Oak Creek Watershed is located in the Sulphur River Basin in Northeast Texas (Figure 1). The soils of this area are dominated by dark brown and dark grayish brown alfisols of two main soil series (1) Nahatche series, a poorly drained loam-silty clay loam soil, moderately permeable, frequently flooded, and typical of flood plains in the region; and (2) Estes series, a somewhat poorly drained clay loam, very slowly permeable, frequently flooded, and typical of flood plains in the region (NRCS, 1990). Soils of the Nahatche series are fine-loamy, siliceous, nonacid, thermic Aeric Fluvaquents. Soils of the Estes series are fine, montmorillonitic, acid, thermic Aeric Haplaquepts. Both soil series were formed in clayey and loamy alluvial sediments over Wilcox and Midway geologic groups of the Paleocene era. The Wilcox Formation, which is prevalent across the entire watershed, consists of cross-bedded layers of shale, lignite, and sand. Medium to very fine quartz sand constitutes about half of the Wilcox group. Sands and shales in the Wilcox group are typically light gray in color. The Midway Formation is the other dominant geologic formation in the watershed. This formation consists mainly of calcareous clay and is impermeable in nature (Figure 2). The climate for the region is humid subtropical having a mean annual temperature of 17°C and annual precipitation of 1,200 mm. Precipitation is distributed fairly evenly throughout the year. Livestock, timber, poultry, and dairy farming are the major agricultural enterprises in the area.

2.2 Sampling Sites and Their Land Use

White Oak Creek watershed (TCEQ Segment 0303B) spans across Hopkins, Franklin, Titus, and Morris Counties in Northeast Texas (eastern point N 33°15'49.92" W 94°44'32.05" and western point N 33°10'43.35" W 95°35'23.58"). The extent of White Oak Creek has been identified as having surface water impairment due to bacteria (Category 5b) since 2006, and depressed dissolved oxygen (Category 5b) since 2000 by the Texas Commission for Environmental Quality (TCEQ 2010b). White Oak Creek is listed in Appendix D of the Texas Surface Water Quality Standards as a perennial stream with an intermediate aquatic life use with an average dissolved oxygen (D.O.) standard of 4.0 mg/L. The stream's designation on the 303(d) list identifies it as unable to meet this criterion. Category 5b designation on the 303(d) list indicates that "a review of the water quality standards for this water body will be conducted before a Total Maximum Daily Load (TMDL) is scheduled (TCEQ 2010b)."

Eighteen tributary or main stem sites were sampled within the watershed over a 1-year period, April 2010 through March 2011. Three of the sites were on the main stem of White Oak Creek, and the remaining 15 were taken from sub-catchments off of the main stem when flow permitted (Figure 1).

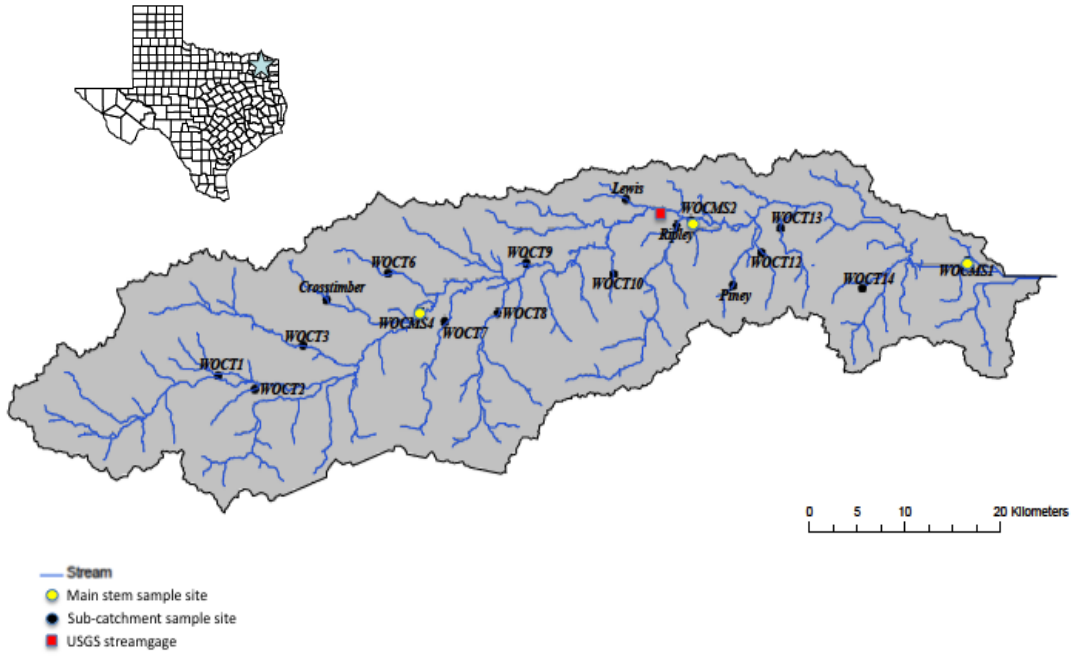


Figure 1. Sampling sites on the main stem and tributaries of White Oak Creek.

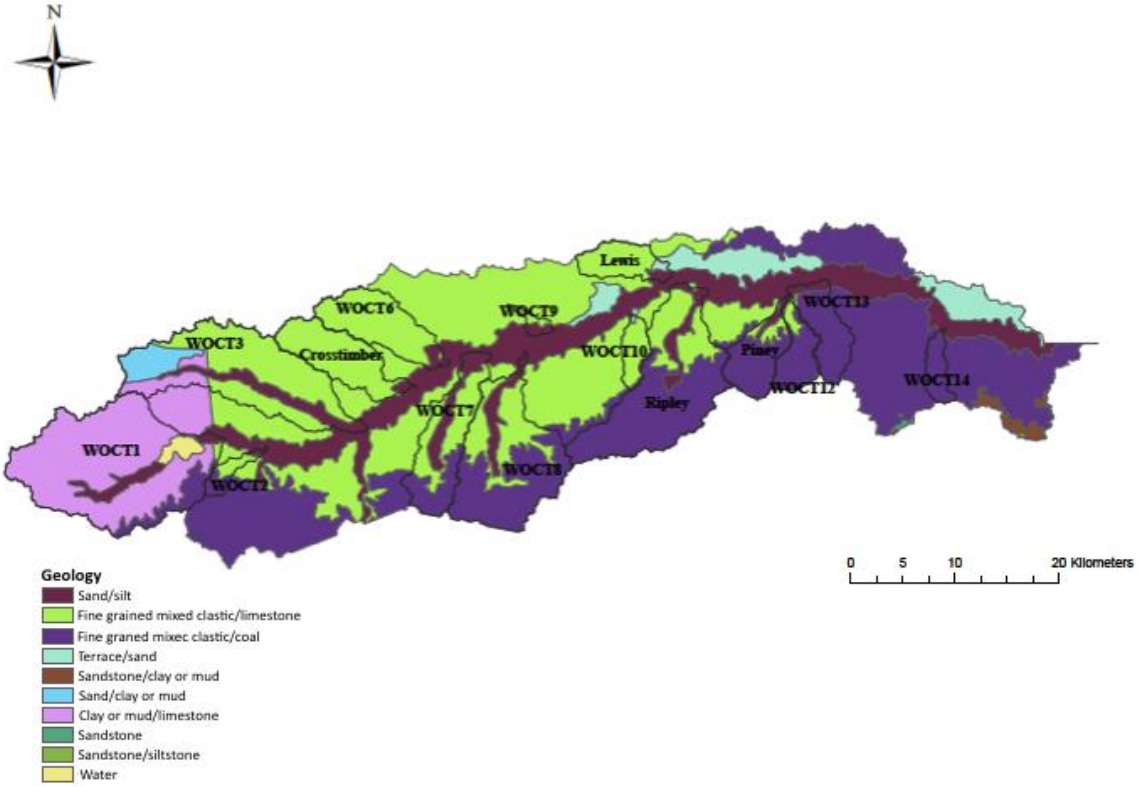


Figure 2. White Oak Creek geology and sub-catchments

Table 1. Coordinates and percent land use in the main stem watersheds. Source of data: NLCD (2001).

Site	Coordinates		Area	Open Water	Developed, Open Space	Developed, Low Intensity	Developed, Med Intensity	Developed, High Intensity	Total Urban	Barren Land	Deciduous Forest	Evergreen Forest	Mixed Forest	Shrub/Scrub	Pasture/Hay	Cultivated Crops	Wetlands
				%													
	N	W	(km^2)														
WOCMS1	33°16’27.60”	94°44’30.05”	1968	1.2	1.2	5.0	0.4	0.2	6.8	0.1	16.6	0.7	0.1	4.5	50.7	6.0	13.5
WOCMS2	33°18’49.45”	95°03’16.38”	1556	1.2	1.3	5.4	0.5	0.2	7.4	0.1	13.2	0.2	0.1	3.8	54.8	7.3	12.1
WOCMS3	33°14’06.58”	95°21’38.31”	772	1.6	1.6	6.1	0.7	0.4	8.8	0.1	11.0	0.1	0.1	2.2	56.3	10.0	10.0

Table 2. Coordinates of sample sites and percent land use in the sub-catchments. Source of data: NLCD (2001)

Site	Coordinates		Area	Open Water	Developed, Open Space	Developed, Low Intensity	Developed, Med Intensity	Developed, High Intensitv	Total Urban	Barren Land	Deciduous Forest	Evergreen Forest	Mixed Forest	Shrub/Scrub	Pasture/Hay	Cultivated Crops	Wetlands
				%													
	N	W	(km^2)														
WOCT1	33°10'48.58"	95°35'23.26"	196	4.0	1.8	6.9	1.0	0.4	10.0	0.1	10.4	0.2	0.1	1.6	56.4	10.5	6.8
WOCT2	33°10'06.05"	95°32'53.99"	10	0.7	4.4	35.0	8.5	4.3	52.2	0.0	7.9	0.0	0.1	1.4	33.2	2.4	2.1
WOCT3	33°12'24.15"	95°29'36.96"	142	0.5	1.0	4.0	0.0	0.0	5.0	0.0	8.6	0.1	0.0	1.6	61.6	12.4	10.2
WOCT6	33°16'09.40"	95°23'49.81"	55	0.7	0.7	4.2	0.0	0.0	4.9	0.0	20.3	0.2	0.2	8.8	52.6	3.6	8.8
WOCT7	33°13'31.06"	95°19'57.83"	66	0.6	0.6	4.5	0.1	0.0	5.1	0.2	14.7	0.2	0.1	4.1	55.0	5.9	14.2
WOCT8	33°14'32.00"	95°16'21.39"	123	0.9	1.0	6.4	0.7	0.2	8.2	0.0	11.4	0.5	0.1	2.4	65.8	5.2	5.6
WOCT9	33°13'38.48"	95°13'28.87"	5	1.0	0.2	3.8	0.2	0.0	4.2	0.0	12.3	0.5	0.2	13.1	37.4	0.0	31.2
WOCT10	33°16'12.36"	95°10'45.60"	15	4.0	1.2	2.3	0.1	0.0	3.5	0.0	14.7	0.1	0.0	3.6	53.6	12.2	8.3
WOCT12	33°17'03.29"	94°58'30.04"	26	1.5	0.5	3.8	0.4	0.1	4.8	2.4	28.5	3.5	0.2	13.3	30.6	6.5	8.9
WOCT13	33°18'21.19"	94°57'11.33"	35	0.6	0.7	3.8	0.0	0.0	4.4	0.0	30.0	3.5	0.4	6.1	38.7	0.8	15.4
WOCT14	33°15'06.81"	94°51'41.72"	14	0.7	0.7	3.4	0.1	0.0	4.1	0.0	42.0	1.4	0.1	9.9	30.8	0.0	11.0
Crosstimber	33°14'47.01"	95°28'00.56"	52	1.1	0.8	3.4	0.0	0.0	4.2	0.0	14.4	0.1	0.1	3.4	57.0	9.1	10.5
Lewis	33°19'57.33"	95°07'40.11"	27	0.6	1.4	7.1	0.0	0.0	8.6	0.0	24.9	0.1	0.0	12.5	34.8	3.9	14.5
Piney	33°15'21.17"	95°00'27.40"	37	0.8	0.7	5.3	0.3	0.1	6.4	0.6	26.9	3.4	0.1	6.1	42.9	6.4	6.5
Ripley	33°18'29.86"	95°04'15.16"	135	1.1	1.6	5.1	0.3	0.1	7.0	0.1	14.2	0.5	0.1	2.5	59.6	3.4	11.6

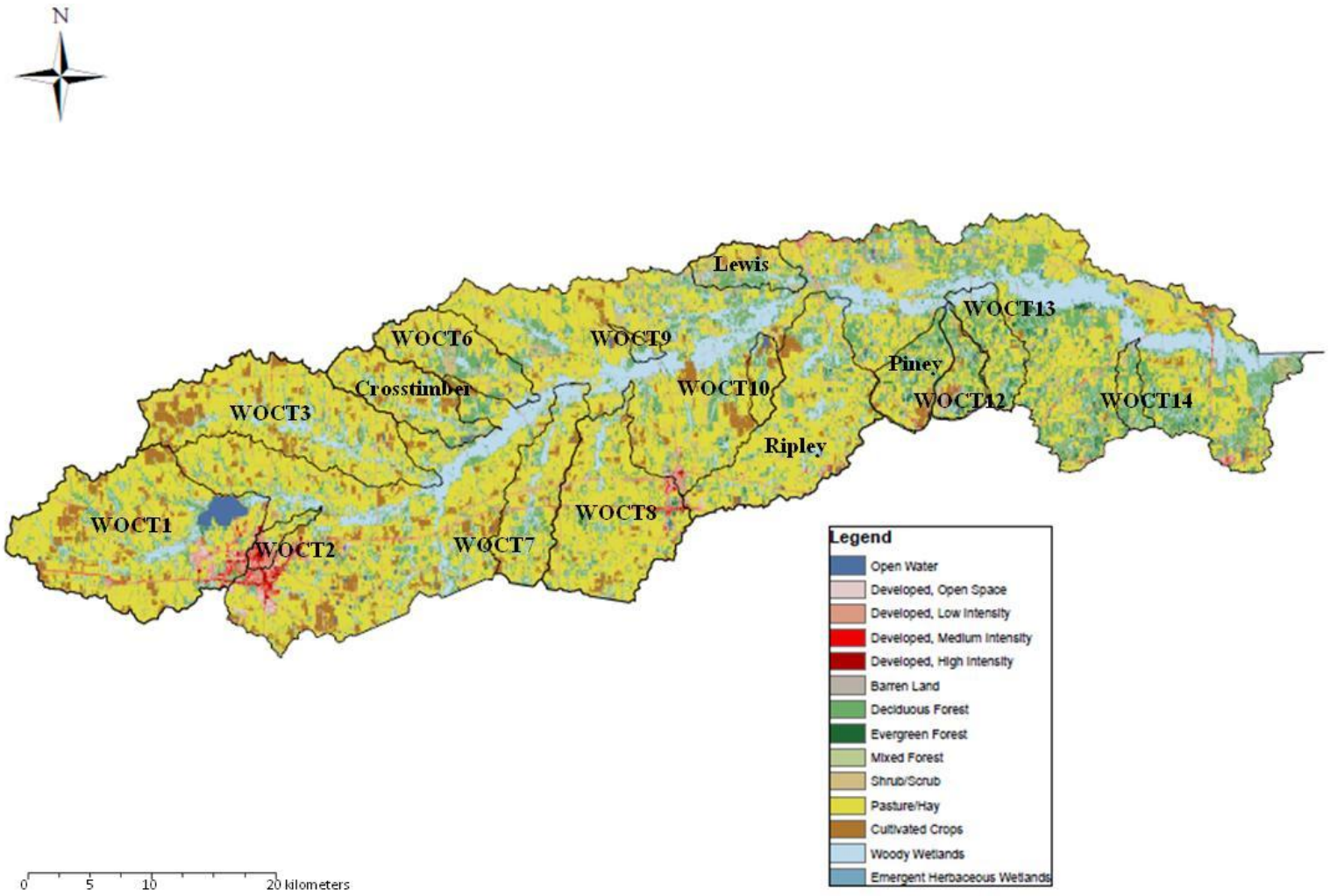


Figure 3. White Oak Creek Watershed land use/land cover within sub-catchments analyzed. Source: NLCD 2001.

2.2.1 Main Stem

Approximately fifty percent of White Oak Creek Watershed is used for pasture/hay land with less than six percent characterized as having some degree of urban/residential development. The remaining land use in the watershed is comprised of forest, wetlands, and shrub/scrub (Table 1, Figure 3). The cities of Sulphur Springs and Mount Vernon located in the south-eastern and central region of the watershed have wastewater treatment facilities that discharge into tributaries of White Oak Creek before joining the main stem (USEPA 2011). Luminant Monticello-Thermo Mine also has permitted wastewater discharge below the city of Sulphur Springs within the watershed that also runs into White Oak Creek. There are also a number of dairy farms permitted to discharge into tributaries within the watershed (USEPA 2011).

2.2.2 Sub-catchments

The headwaters of White Oak Creek originate approximately twelve miles west of the city of Sulphur Springs. The first sampling site (WOCT1) at its headwaters was taken north of the city on highway 19/154 on the main stem of the creek. Despite its proximity to the city, WOCT1 is largely pastured land and forest, encompassing only the western most portion of the City of Sulphur Springs. WOCT1 sub-catchment drains an approximate area of 196 km^2 (Table 2, Figure 3). Northwest of the city, White Oak Creek is dammed to form a 1,340 acre impoundment, Lake Sulphur Springs, for the city's backup water supply.

Sub-catchment WOCT2 is the most developed of the sampling sites with its headwaters forming in the most developed area of the entire watershed, which graduates

to pasture/hay land before merging with White Oak Creek. Drainage area is 10 km^2 for this sub-catchment (Table 2).

WOCT3 has the highest percentage of cultivated crops out of all the sub-catchments, in addition to over sixty percent pasture and hay land cover. The remaining land use is comprised mainly of forest and wetlands. WOCT3 is one of the largest sub-catchments draining approximately 142 km^2 (Table 2). Similarly, the adjacent sub-catchment, Crosstimber, also follows this land use pattern with higher percentages of cultivated crops, pasture, forest, and wetland, although its drainage area is only 52 km^2 (Table 2).

Sub-catchments WOCT6, on the north side of White Oak Creek, and WOCT7 on the south side of White Oak Creek are also similar in that the largest proportion of land use is contributed to pasture and hay land cover. WOCT6 and WOCT7 drain areas of 55 km^2 and 66 km^2, respectively (Table 2). WOCT7 has two registered dairy farms permitted for discharge into the tributaries of this catchment (USEPA 2011).

The adjacent sub-catchment on the south side of White Oak Creek, WOCT8, contains the largest percentage of pasture hay land cover in the watershed, and drains an area of 123 km^2 (Table 2). A small portion of the headwaters for this catchment begin in low-intensity development areas at the City of Mount Vernon. The city of Mount Vernon wastewater treatment facility discharges into the tributaries of this catchment. One registered dairy farm is permitted to discharge in this sub catchment.

WOCT9 is a small sub-catchment draining 5 km^2. One third of its area is characterized as woody wetlands, while another third is pastured land, and the remaining

is forest and shrub/scrub land. Similarly, WOCT10 another smaller sub-catchment with a drainage area of 15 km^2 consists of pastured land and forest with some cultivated crops, but also contains a higher percentage of open water (Table 2).

On the northern side of White Oak Creek towards the middle of White Oak Creek Watershed, the Lewis Creek sampling site is a sub-catchment that consists of a higher proportion of wetlands than most other catchments. It is also mixed with deciduous forest, pasture, and scrub land (Table 2).

Ripley Creek sub-catchment has the second largest drainage area of all the sampling sites with 135 km^2. Its headwaters begin near the city of Mount Vernon and flow northeast into White Oak Creek. Nearly sixty percent of the sub-catchment area is used as pasture land, while the remaining is composed of deciduous forest, woody wetlands, and low intensity development (Table 2). A portion of the headwaters in the southeastern area of the catchment is located in a reclaimed lignite coal surface mine site.

Adjacent sub-catchments Piney and WOCT12 merge before flowing into White Oak Creek. Similar to Ripley catchment, both Piney and WOCT12 headwaters form in an area that was previously used for lignite coal surface mining. Much of the area is now reclaimed land. In the Piney sub-catchment forty-three percent is used for pasture and hay, while the remaining majority is forested land. WOCT12 contains the highest percentage, although minimal, of the classified barren land, largely as a result of mining activities, with the remaining land uses consisting of forested, pasture, shrubs and wetland.

WOCT13 and WOCT14 are the western most sub-catchment sampling sites. A greater proportion of these areas consist of deciduous forest, pasture, and woody wetlands. WOCT14 is located in the protected White Oak Creek Wildlife Management Area.

2.3 Stream Sample Collection

Grab samples were collected from the 18 sampling sites mid-channel and mid depth using 500 mL sterile Whirlpak sample bags (Nasco Co., Modest CA) at least once a month between April 2010 and March 2011. Samples were taken from the upstream side of bridges for ease of sampling. Electrical conductivity and pH were quantified on unfiltered samples and then a portion of each sample was syringe filtered through Whatman GF/F filters (0.7 μm nominal pore size) into acid washed ultra-pure water rinsed HDPE bottles. Further aliquots were filtered through 0.2 μm Pall filters in readiness for cation and anion analysis. These samples were either analyzed on the day of collection or frozen after filtration for later analysis.

2.3.1 Biological Oxygen Demand

Samples for BOD_5 analysis were taken from the 18 sampling sites in 500 mL acid washed, ultra-pure rinsed water high density polyethelene (HDPE) bottles for DO analysis on the day of sampling. BOD samples were analyzed from the 18 sampling sites using 300 mL of stream water poured into acid washed, ultra-pure water rinsed glass BOD bottles. Dissolved oxygen, quantified with a YSI 5000 BOD/DO meter (YSI Inc., Yellow Springs, OH) was recorded at t = 1, and the bottles were incubated at 25 °C for

five days where dissolved oxygen (DO) was recorded again at t = 5. BOD was calculated as the difference of DO at t = 1 and DO t = 5 in mg/L.

2.3.2 Sediment Analysis

Suspended sediments were analyzed by filtering 100 mL of stream water through pre-weighed glass fiber Whatman GF/F filters (0.7 μm nominal pore size). Filters were then placed in the oven at 60 °C for 2 days to evaporate water. Filters were then re-weighed after 2 days and equilibrium with room temperature to determine suspended sediments. Total solids were quantified by weighing 50 mL of stream water into pre-weighed Pyrex® beakers and placed in the oven at 60 °C for 3 days or until evaporation was complete. After cooling to room temperature the beakers were then weighed to determine total solids. Total dissolved solids were calculated as total solids minus suspended solids.

Turbidity was measured in nephelometric turbidity units (NTU) using a Turbidity Meter Model 800 (VWR International, Radnor, PA). The meter was calibrated with solutions of 0 and 10 NTU prior to analysis.

2.3.3 Chemical Analysis

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured using high temperature Platinum-catalyzed combustion with a Shimadzu TOC-VCSH and Shimadzu total measuring unit TNM-1 (Shimadzu Corp. Houston, TX, USA). Dissolved organic carbon was measured as non-purgeable carbon, which entails acidifying the sample (250 μL 2M HCl) and sparging for 4 min with C-free air. Ammonium was analyzed using the phenate hypochlorite method with sodium

nitroprusside enhancement (USEPA method 350.1) and nitrate was analyzed using Cd-Cu reduction (USEPA method 353.3). Alkalinity was quantified using methyl orange (USEPA method 310.2). Alkalinity was converted to the major carbonate species (AqQA, Rockware Inc., Denver, CO), which in this study was bicarbonate. All colorimetric methods were performed with a Westco Scientific Smartchem Discrete Analyzer. Calcium, magnesium, potassium and sodium were quantified by ion chromatography using an Ionpac CS12A analytical and Ionpac CG12A guard column for separation and 20 mM methanosulfonic acid as eluent at a flow rate of 1 mL min^{-1} and injection volume of 25 µL (DIONEX ICS 1000). Fluoride, chloride, bromide, sulfate and phosphate were quantified using Ionpak AS20 and Ionpak AG20 analytical and guard columns for separation with 35 mM KOH as eluent at a flow rate of 1 mL min^{-1} and an injection volume of 25 µL (DIONEX ICS 1000). Dissolved organic nitrogen was estimated by deducting inorganic-N (NH_3-N + NO_3-N) from TDN. NIST traceable check standards and water blanks were analyzed every 12^{th} sample for QA/QC on instrument precision and coefficient of variance between replicates.

2.4 Watershed Delineation and Land Cover Analysis

ArcGIS version 10.0 ESRI 2010 software was used to delineate the watershed and each sub-catchment and to calculate land cover type and geology for each watershed. Watershed delineation was performed using the Hydrology functions under the Spatial Analyst Toolbox in the software. Input data is 30 x 30 m digital elevation model (DEM) raster data, which is publically available from the USGS Seamless (USGS

2011). Geology (USGS 2011) and National Land Cover Data (USEPA 2001) for each watershed was calculated using the *zonal statistics* calculator in the *Spatial Analyst* using data from the USGS Seamless database (USGS 2011). ArcMap's *Spatial Analyst* function was used to estimate the area of each of the land uses within each catchment and watershed as a whole. Land use areas were divided by the catchment and watershed area to derive the percentage of the catchment and watershed covered by each type. All LULC files were cast to the Universal Transverse Mercator (UTM) projection, and referenced to the North American Datum of 1983 (NAD83).

2.5 Load and Export Estimation for White Oak Creek

Two methods of estimating daily load and annual export in White Oak Creek were used. The USGS Gauge 073433500 near Talco (N33° 19' 30" W95° 05' 33' NAD 27) was used for daily discharge during the study period. The first method examined natural log transformed concentrations paired with natural log transformed discharge at the gauge on the days that the sample was collected (Ln-Ln model) and used the paired concentration (mg/L) and discharge (L/sec) in regression analysis to derive an equation that was used to estimate concentrations of chemical constituent on the days that samples were not collected. Natural log concentrations were derived for each day of the sampling period and then re-transformed using their exponential to give an estimation of milligrams per second. These values were then multiplied by 86,400 and divided by 1,000,000 for a load value of kilograms per day. Data were summed for an annual load and divided by the watershed area for annual export ($kg/km^2/yr$). Because not all of the

chemical constituents had a significant positive of negative relationship with stream discharge, a second method of determining daily load and annual export was used. The second method was that of linear interpolation (LI model). Here a regression line is drawn between two collected sample concentrations and the equation derived is used with the number of day (counting 1 though n) as the independent variable (x) to calculate concentrations on those days not sampled. Both methods of determining load and export have been published (e.g. Steele and Aitkenhead-Peterson 2011; Petrone 2010).

2.6 Statistical Analysis

Data was examined for normality and transformed prior to statistical analysis if necessary. Annual and seasonal means of each stream chemical constituent were calculated and student's two-tailed t-tests were used to test the null hypothesis that the stream chemistries for the main stem and sub-catchments were not significantly different. Correlation analysis was used to test the hypothesis that high sediments would result in low dissolved oxygen within each individual sub-catchment and to examine correlations between land use and water chemistry and between stream chemistries in the sub-catchments. Annual mean stream chemical constituents were used in regression analysis with watershed land use to examine relationships with any specific land uses. All statistical analysis was performed using SPSS v. 16.

3. RESULTS

3.1 Mean Annual Surface Water Chemistry: Sub-catchments

There were no significant differences in mean annual surface water pH in the White Oak Creek sub-catchments (Figure 4A). Mean annual surface water pH ranged from 6.94±0.29 to 7.37±0.39. Electrical conductivity (EC) was however significantly different among the sub-catchments. WOCT8 and WOCT13 had significantly higher EC than all the other streams with the exception of WOCT9, WOCT 7, WOCT 14, Ripley and Piney (Figure 4B). Mean annual surface water EC ranged from 146±64 to 638±198 $\mu S\ cm^{-1}$.

Although White Oak Creek is on the TCEQ 303(d) list for low oxygen. The mean annual DO concentrations were above 4 mg/L at all the sampling sites. Lowest DO concentration was found in WOCT12 at 7.32±0.75 mg/L and the highest DO at WOCT9 at 8.25±0.38. There was no significant difference in surface water DO among the sub-catchments (Figure 5). Biological oxygen demand in the sub-catchments was minimal and ranged from 0±0 to 2.1±1.9 mg/L the lowest BOD_5 was at sub-catchments Lewis and WOCT7 and the highest BOD_5 was at WOCT3 (data not shown).

All nitrogen and soluble phosphorus nutrients were significantly different among the sub-catchments and the same general sub-catchments were responsible for the highest mean annual concentrations of N and P. Significantly higher annual mean ammonium-N concentrations were found at WOCT2 relative to all the other sub-catchments with the exception of Lewis and WOCT8. Mean annual ammonium-N concentrations at WOCT2 were 0.32±0.31 mg/L. Lowest ammonium-N concentrations were found for WOCT14 at 0.09±0.03 mg/L but the concentrations were not significantly lower than any of the other sub-catchments with the exception of WOCT2 (Figure 6A). Mean annual nitrate-N concentrations ranged from 0.13±0.08 to 0.97±0.89 mg/L.

Lowest nitrate-N concentrations were at Piney and the highest were at WOCT2 (Figure 6B). WOCT2 had significantly higher mean annual nitrate-N concentrations relative to all the other sub-catchments with the exception of WOCT7 and WOCT9 (Figure 6B). Soluble phosphorus, quantified as othophosphate-P was highest at WOCT7 where it was significantly higher in concentration than all the other sub-catchments except WOCT2. Mean annual soluble phosphorus ranged from 0.03±0.02 to 0.44±0.74 mg/L (Figure 7A).

Alkalinity quantified as $CaCO_3$ was not significantly different among the sub-catchments and mean annual concentrations ranged from 36.9±16.4 to 104.8±61.4 mg/L the lowest alkalinity was in WOCT10 and the highest in WOCT7 (Figure 5B).

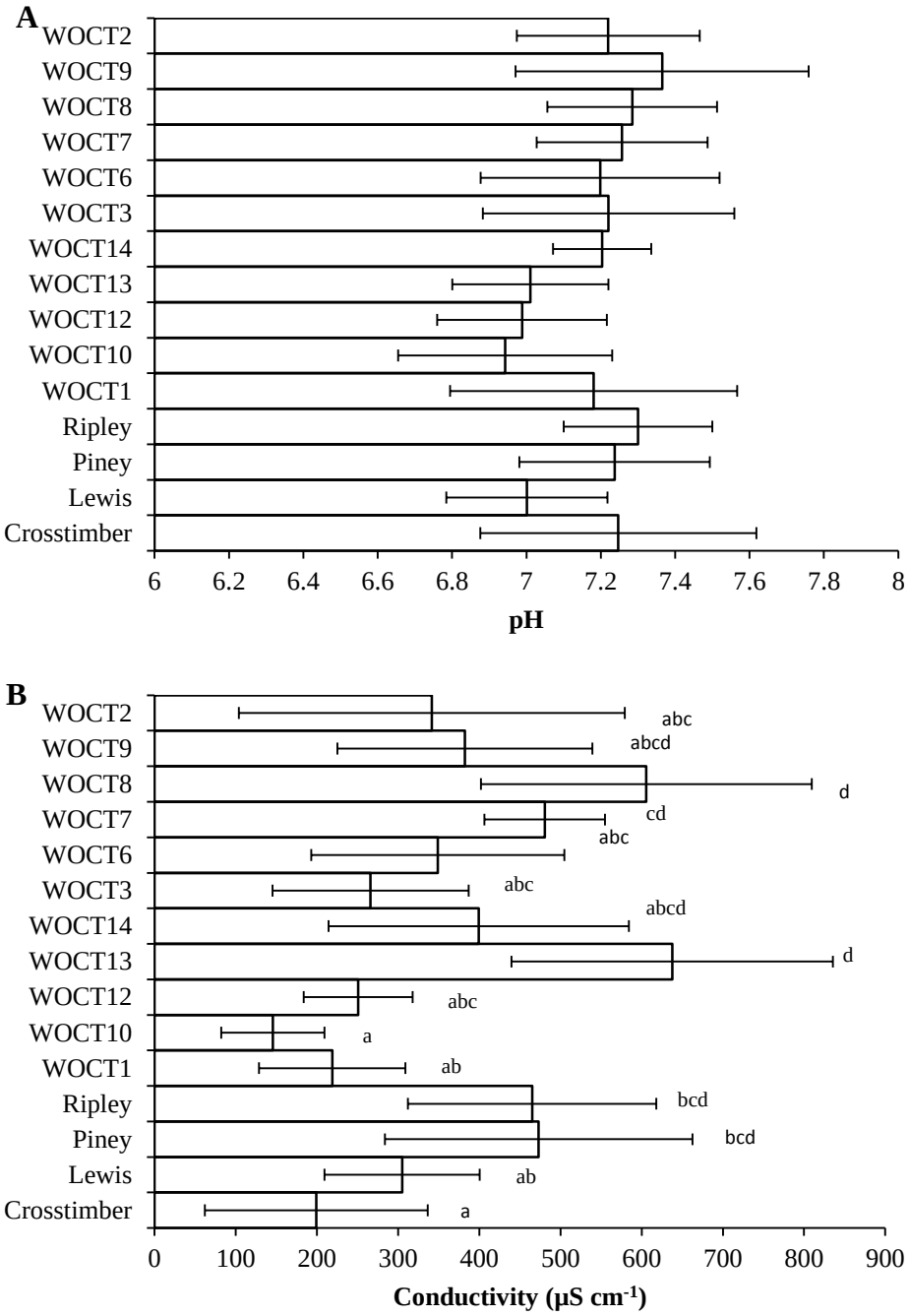


Figure 4. A) pH and B) electrical conductivity of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. No letters indicate there was no significant difference (pH). Error bars are standard deviation.

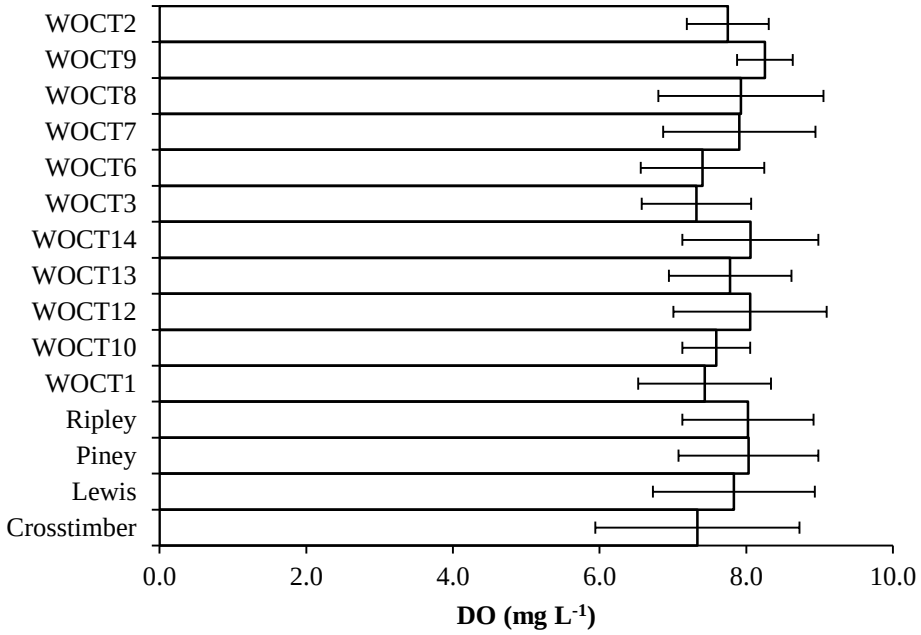


Figure 5. Dissolved oxygen concentrations in the eighteen sub-catchments. Error bars are standard deviation.

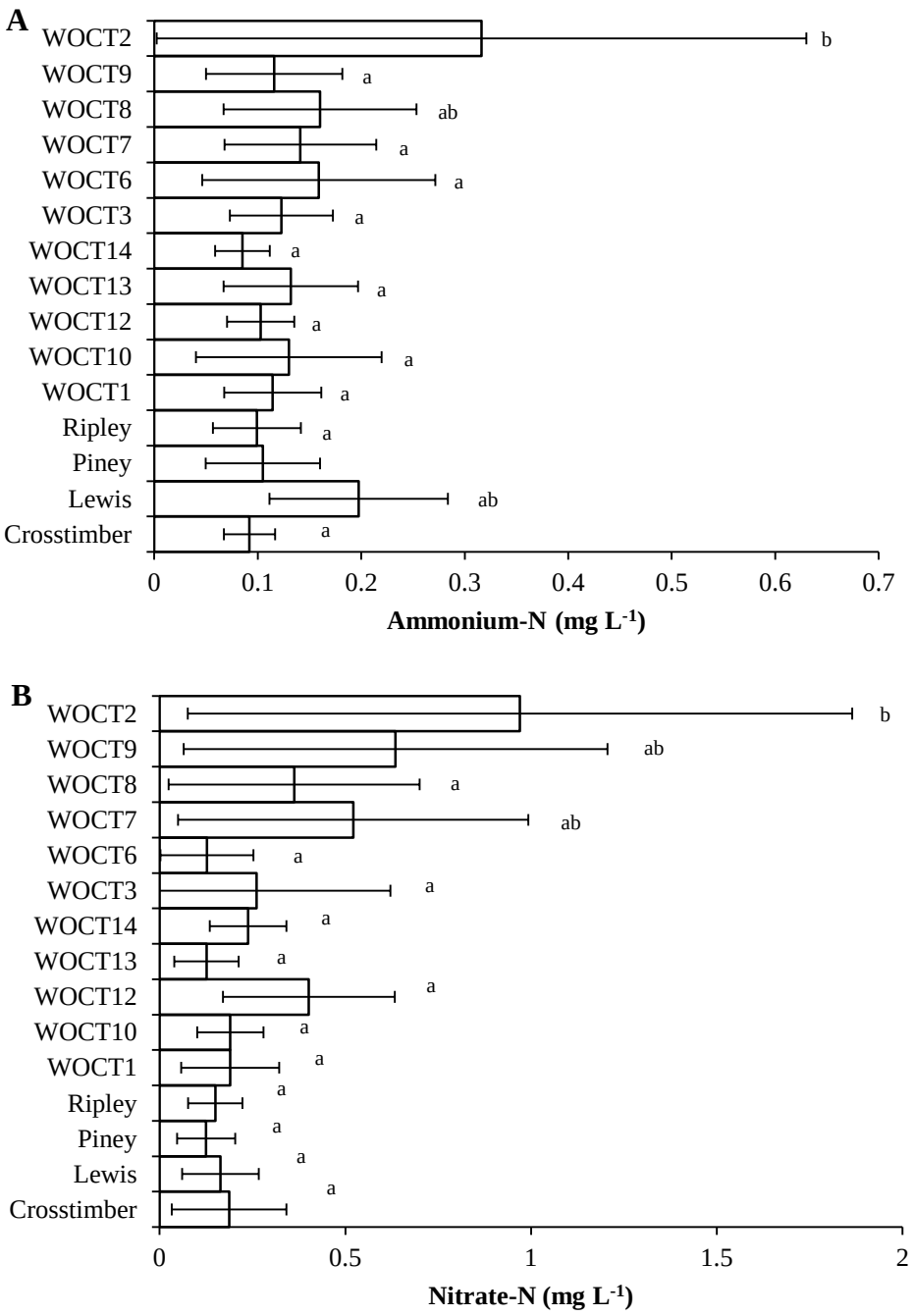


Figure 6. A) Ammonium-N and B) nitrate-N concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. Error bars are standard deviation.

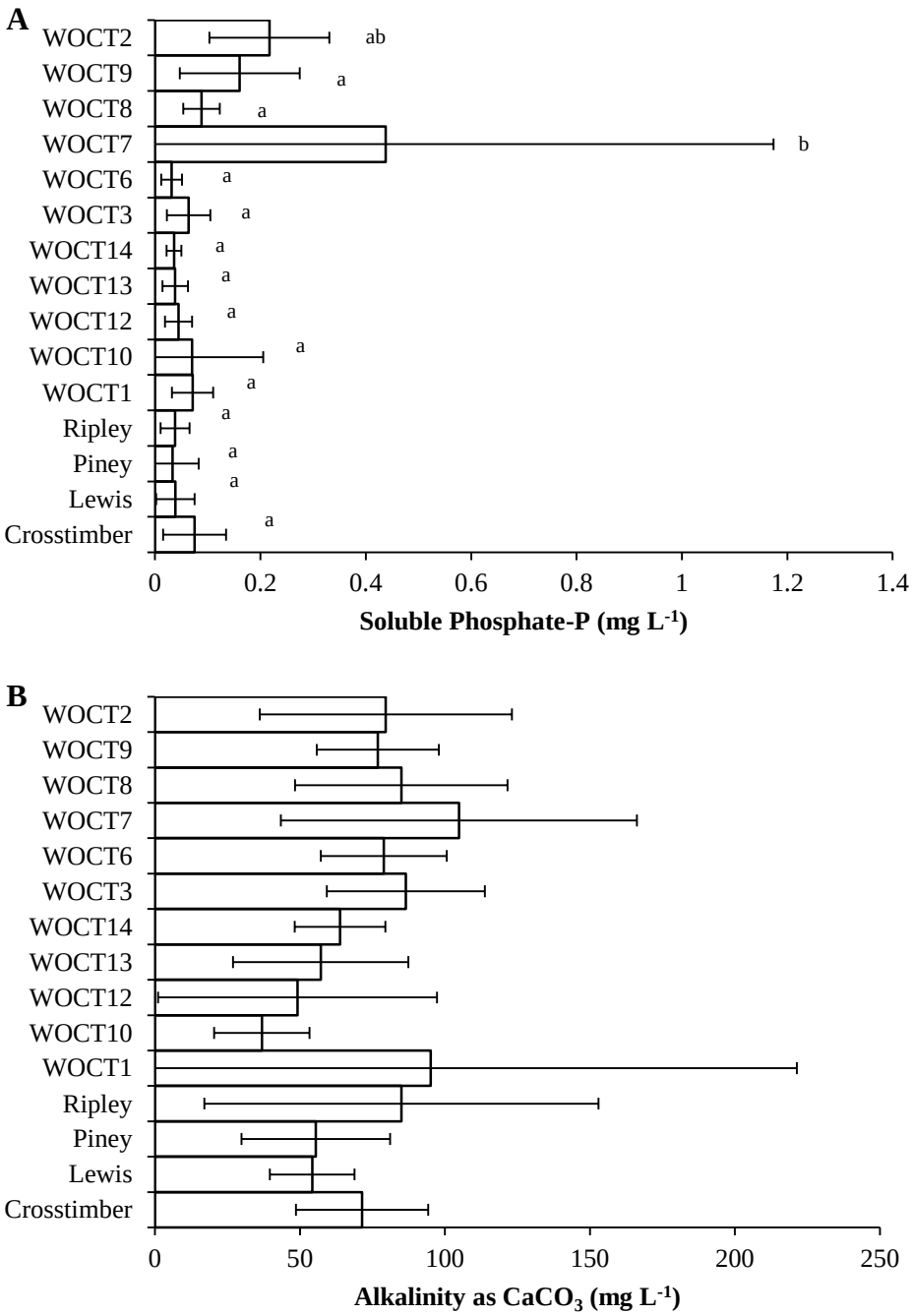


Figure 7. A) Soluble phosphate-P and B) alkalinity measured as $CaCO_3$ concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. No letters indicate there was no significant difference (Alkalinity). Error bars are standard deviation.

Mean annual cation concentrations were significantly different among the White Oak Creek sub-catchments. Sodium concentrations ranged from 18.6±8.02 to 53.6±17.14 mg/L. The highest sodium concentrations were in WOCT8 and here sodium concentrations were significantly higher than all the other sub-catchments with the exception of WOCT7, WOCT14, WOCT9, Piney, WOCT13 and Ripley. The lowest mean annual sodium concentration was in Crosstimber where it was significantly lower than WOCT14, WOCT9, Piney, WOCT13 and Ripley sub-catchments. (Figure 8A).

Potassium concentrations ranged from 3.89±1.34 to 12.07±3.49 mg/L. The highest potassium concentrations were found in WOCT7 where they were significantly higher than all the other sub-catchments and the lowest in WOCT14 where they were significantly lower than in WOCT7, WOCT8, WOCT9 and WOCT2 (Figure 8B).

Magnesium and calcium concentrations in the sub-catchments ranged from 4.87±1.83 to 12.30±3.73 mg/L and 11.68±3.97 to 26.48±15.59 mg/L, respectively. Lowest mean annual magnesium concentrations were found in WOCT1 and highest in WOCT8. Lowest mean annual calcium concentrations were found in WOCT10 and highest in WOCT2 (Figure 9B). WOCT1 had significantly lower magnesium concentrations relative to WOCT8, WOCT7, WOCT13, and Piney, and WOCT8 had significantly higher magnesium concentrations compared to WOCT14, Ripley, WOCT7, WOCT13, and Piney (Figure 9A).

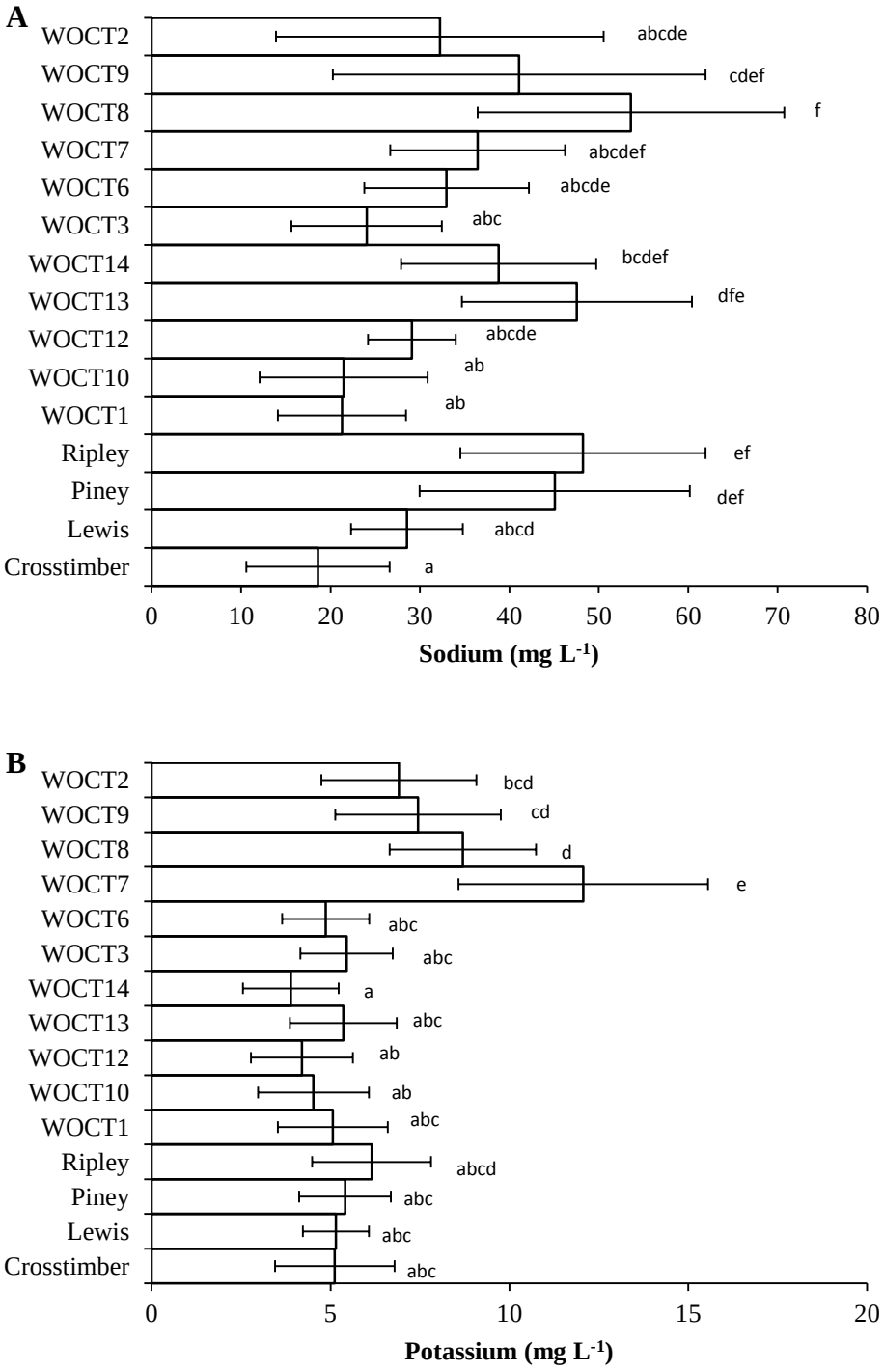
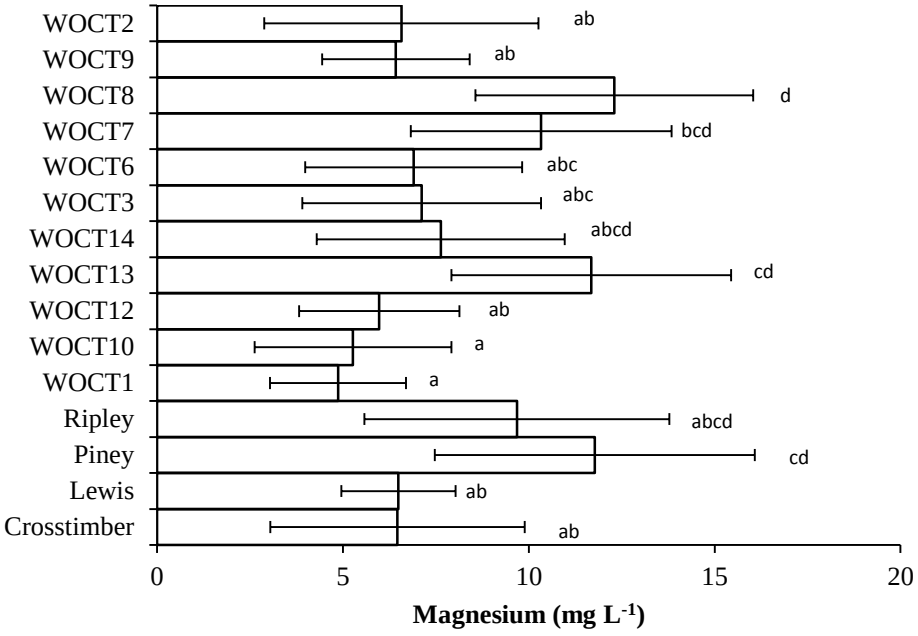


Figure 8. A) Sodium and B) potassium concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. Error bars are standard deviation.



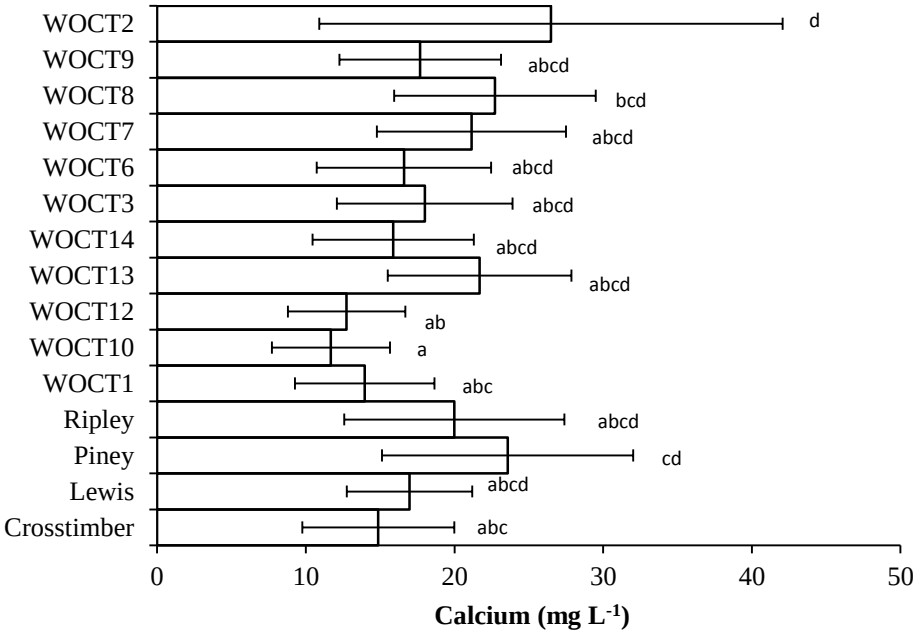


Figure 9. A) Magnesium and B) calcium concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. Error bars are standard deviation.

Mean annual anion concentrations, fluoride, chloride and sulfate showed significant differences in concentrations among the sub-catchments. Mean annual fluoride concentrations ranged from 0.09±0.06 mg/L to 0.41±0.28 mg/L. Lowest fluoride concentrations were found at WOCT12, while the highest were found at WOCT2 (Figure 10A). Sub-catchment WOCT2 had significantly higher mean annual fluoride concentrations than the other sub-catchments, with the exception of WOCT9 and WOCT3 (Figure 10A). Chloride concentrations varied widely among the sub-catchments (Figure 10B). Mean annual chloride concentrations ranged from 11.82±4.37 mg/L at sub-catchment WOCT10 to 53.19±16.00 mg/L at sub-catchment WOCT8. WOCT10 had significantly lower chloride concentrations relative to WOCT8, WOCT7, WOCT6, WOCT14, WOCT13, Ripley, and Piney. While WOCT8 and WOCT13 had significantly higher chloride concentrations than all the other streams with the exception of WOCT9, WOCT7, WOCT6, WOCT14, Ripley, Piney, and Lewis (Figure 10B).

Mean annual sulfate concentrations were significantly different among the White Oak Creek sub-catchments (Figure 11). Sulfate concentrations ranged from 17.42±13.31 mg/L to 104.40±44.40 mg/L. Lowest mean annual sulfate concentrations were found in Crosstimber, while highest mean annual concentrations were found in Piney. Piney had significantly higher sulfate concentrations when compared to the other streams with the exception of WOCT8, WOCT13, and Ripley (Figure 11).

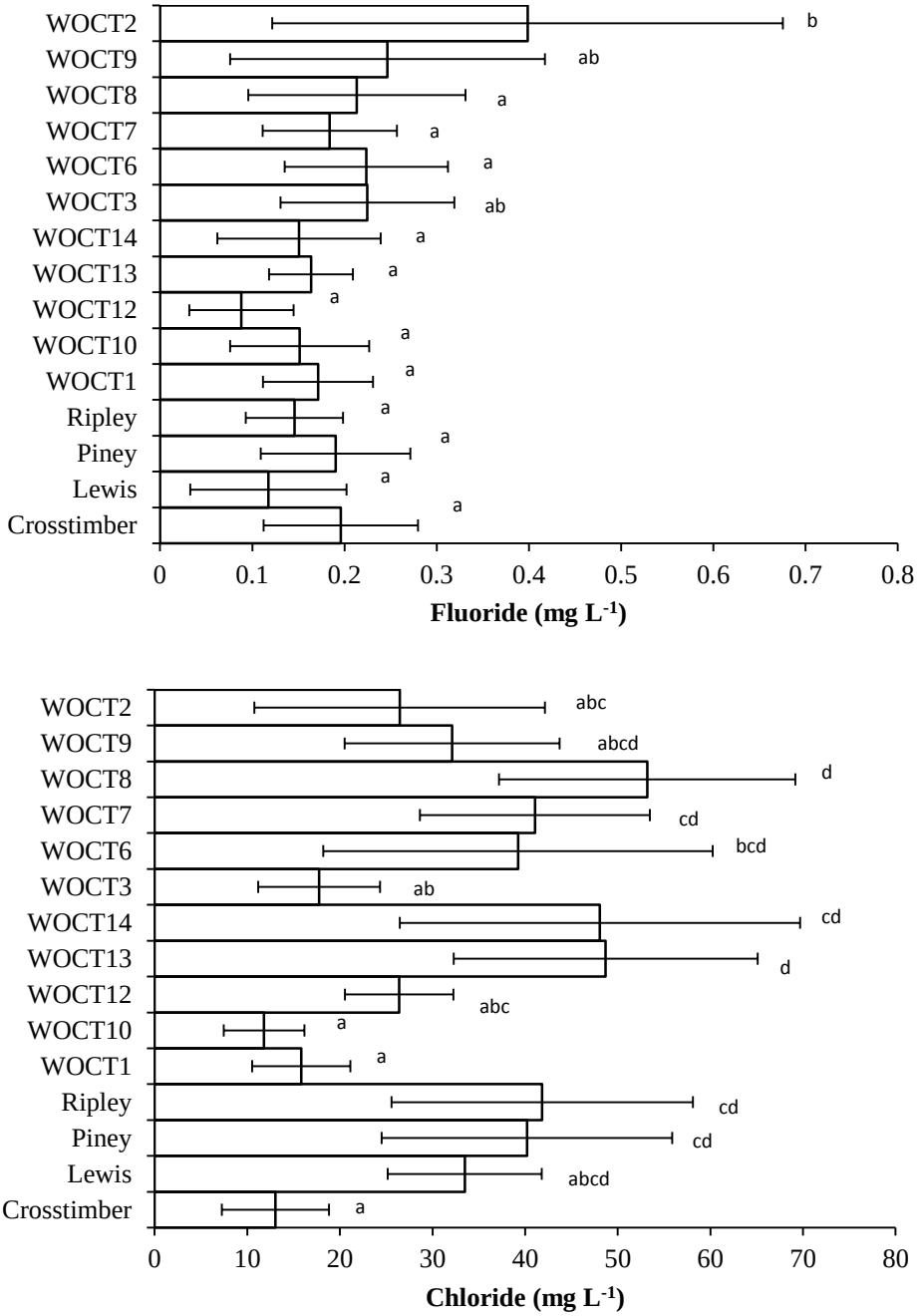


Figure 10. A) Fluoride and B) chloride concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. Error bars are standard deviation.

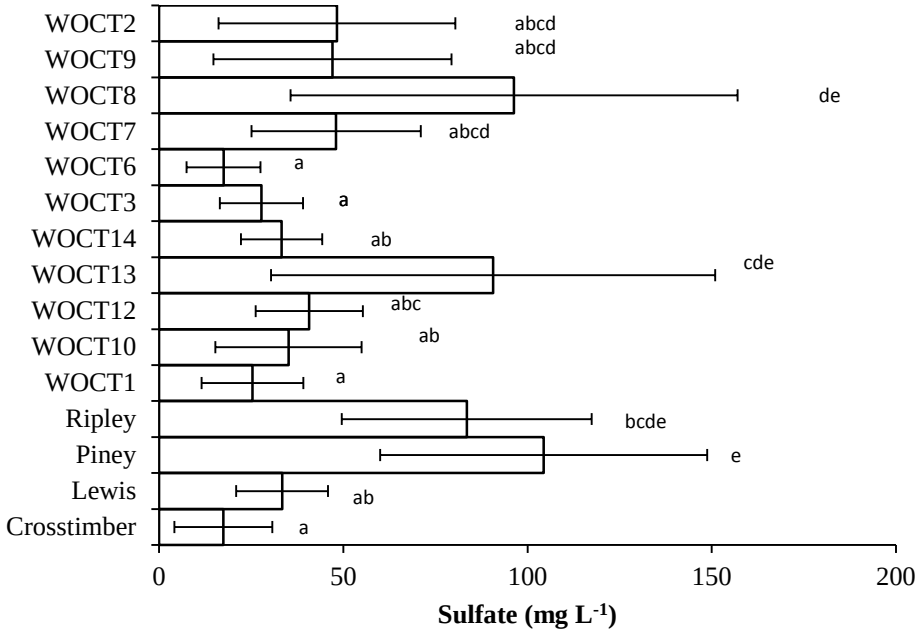


Figure 11. Sulfate concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. Error bars are standard deviation.

Mean annual concentrations of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) ranged from 6.03±2.02 mg/L to 14.66±2.49 mg/L and 0.18±0.09 to 0.68±0.07 mg/L, respectively (Figures 12 A& B). Lowest mean annual DOC concentrations were found in WOCT14 and highest in Lewis. Lowest mean annual DON concentrations were found in WOCT12 and highest in WOCT7. Lewis had significantly higher DOC concentrations when compared to the other tributaries (Figure 12A). WOCT7 and Crosstimber had significantly higher DON concentrations particularly when compared to WOCT8, WOCT3, and Lewis (Figure 12B).

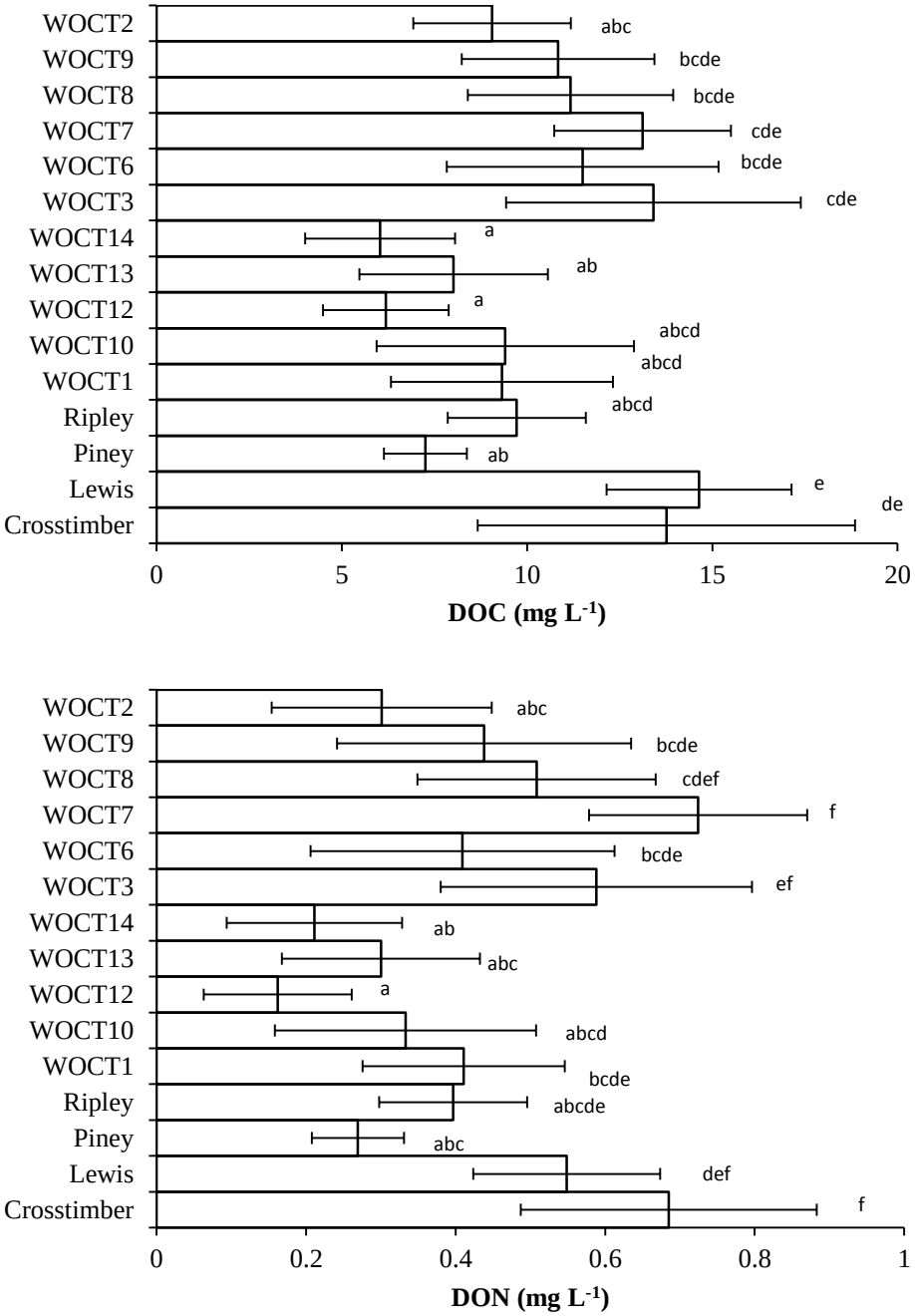


Figure 12. A) Dissolved organic carbon (DOC) and, B) dissolved organic nitrogen (DON) concentrations of samples taken from the White Oak Creek sub-catchments. Differences in lower-case, superscript letters indicate a significant difference at $\alpha < 0.05$ and similar letters indicate no significant difference between streams. Error bars are standard deviation.

3.2 Mean Annual Surface Water Chemistry: Main Stem

Three sites along the main stem were sampled during my study period. WOCMS4 is the first 1/3rd of the basin downstream from eight of the sub-catchments, WOCMS2 is approximately center of White Oak Creek basin and is just downstream of a USGS gauge and WOCMS1 is the main stem prior to its confluence with Sulphur River (Figure 2). Measurements of pH were not significantly different along the main stem and ranged from 7.2 to 7.4 (Figure 13A). There was a significant difference among the main stem sampling sites for electrical conductivity with WOCMS4 having significantly higher conductivity relative to WOCMS1 (Figure 13B).

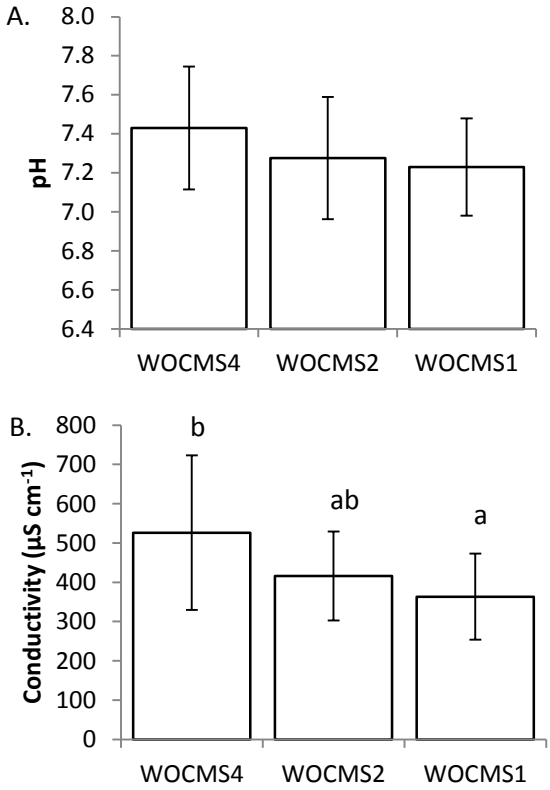


Figure 13. A) pH and B) electrical conductivity of the main stream sampling sites. Error bars are standard deviation.

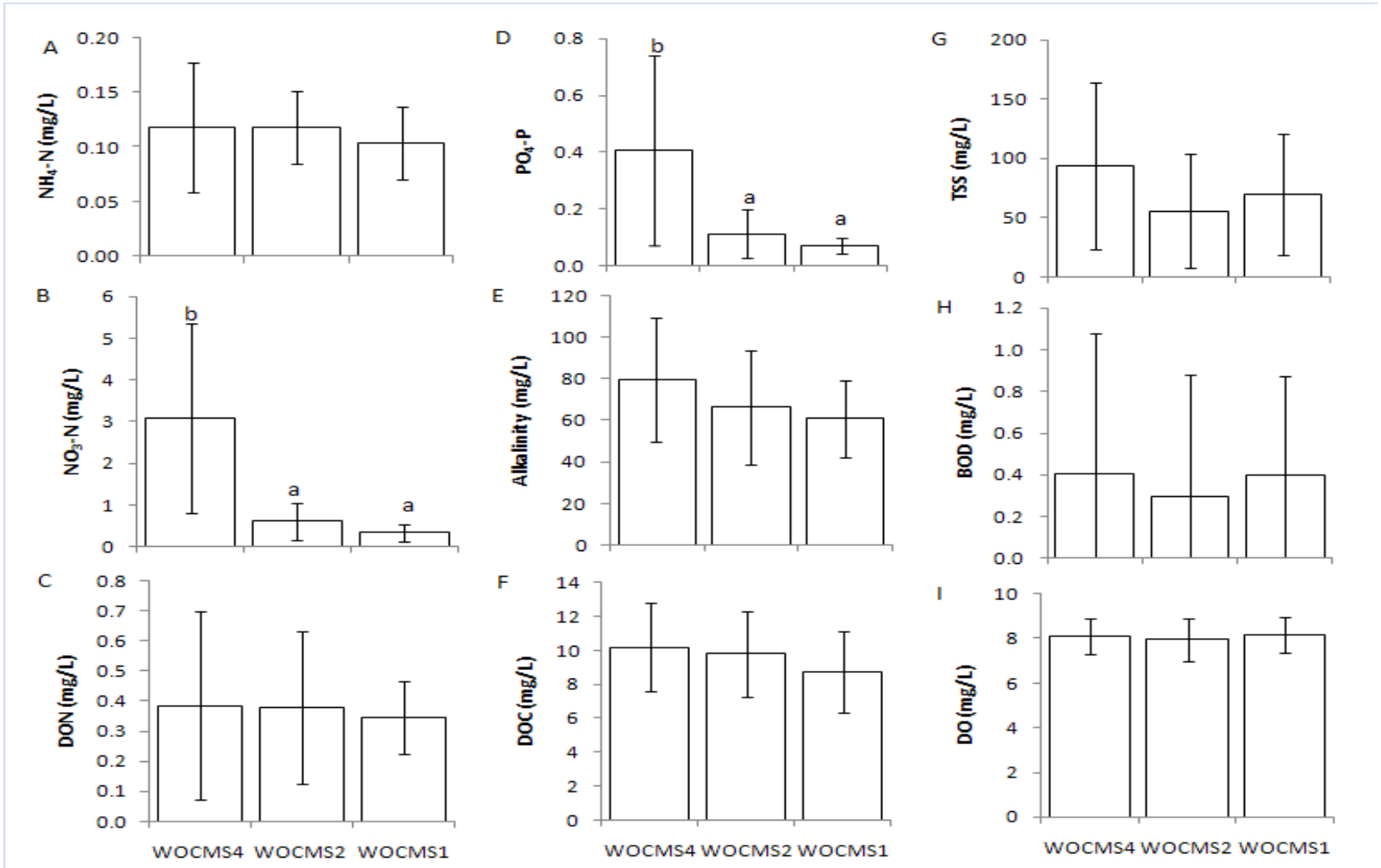


Figure 14. Nutrients, carbon and measures of total suspended solids, DO and BOD along the main stem. Error bars are standard deviation. Significant differences ($p < 0.05$) are shown by different lower case letters. Figures with no letters have no significant difference.

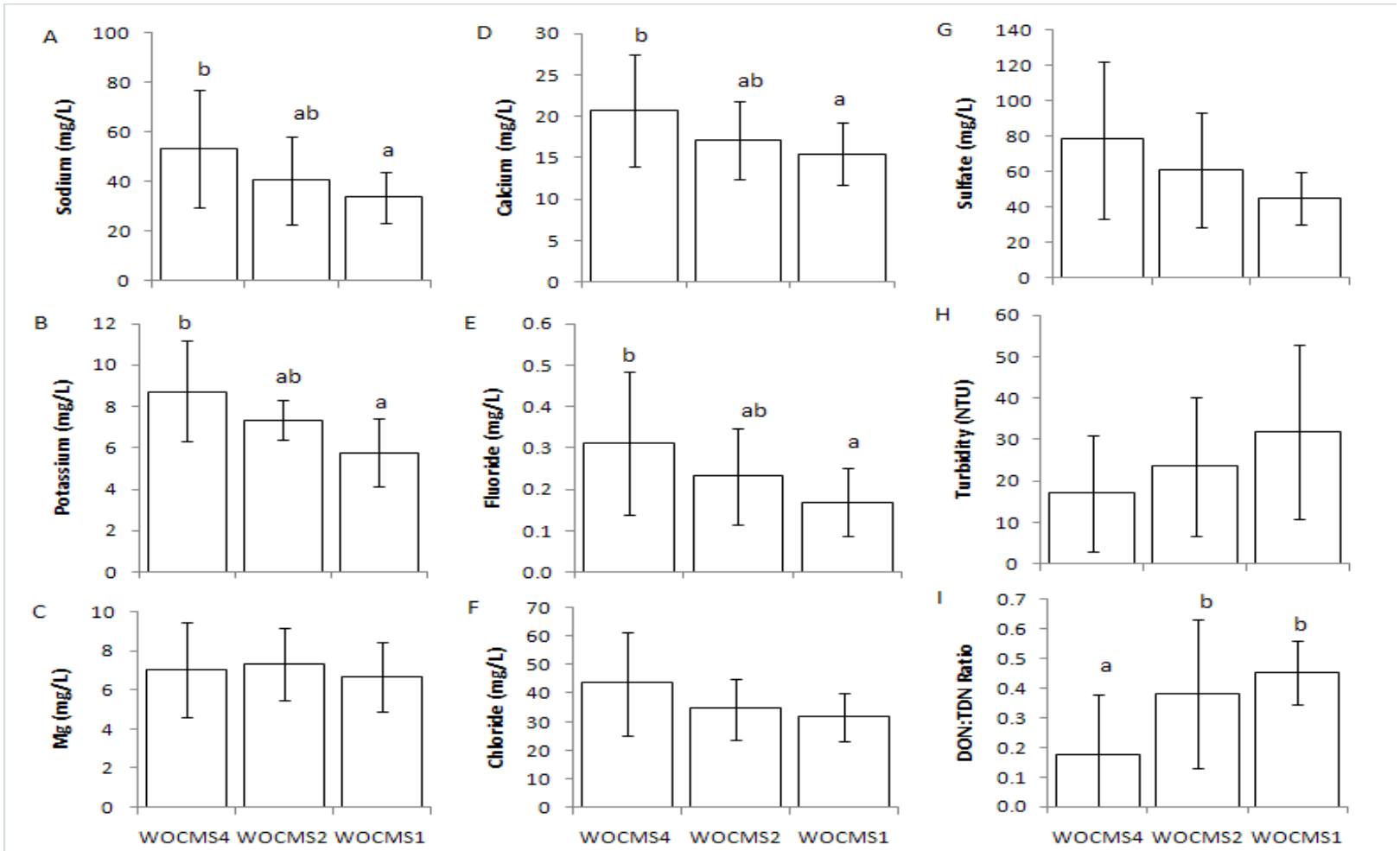


Figure 15. Cations, anions and DON:TDN ratio along the main stem. Error bars are standard deviation. Significant differences ($p < 0.05$) are shown by different lower case letters. Figures with no letters have no significant difference.

Several of the chemical constituents were not significantly different along White Oak Creek main stem and these included Ammonium-N (Figure 14A), Dissolved organic Nitrogen (Figure 14C), Alkalinity (Figure 14E), DOC (Figure 14F), total suspended solids (Figure 14G), biological oxygen demand (BOD), dissolved oxygen (Figures 14H and 14I), magnesium (Figure 15C), chloride (Figure 15F), sulfate (Figure 15G) and turbidity (Figure 15H). Other chemical constituents showed a significant difference along the main stem, and for the most part were all significantly higher at WOCMS4 and included nitrate-N (Figure 14B), orthophosphate-P (Figure 14D), sodium (Figure 15A), potassium (Figure 15B), calcium (Figure 15D), fluoride (Figure 15E) and the DON:TDN ratio (Figure 15I).

Concentrations of chemical constituents decreased along the main stem, which could be attributed to dilution from the sub-catchments.

3.3 Discharge, Loads and Exports of Nutrients and Chemical Constituents from White Oak Creek Watershed

A total of twelve surface water samples were taken from downstream of the gauge at WOCMS2 throughout the course of the study period which were pretty evenly distributed throughout the year to take account of high and low flow discharge (Figure 16A). One extreme storm event occurred on July 17th, 2010 at Clarkesville, TX approximately 20 miles north of the Talco gauge when 32 mm of precipitation fell (Figure 16B) and one extreme event occurred at Sulphur Springs, TX on November 2nd

2011 when 29 mm rain was recorded (Figure 16B). Several smaller storm events occurred in the watershed throughout the sampling period (Figure 16B).

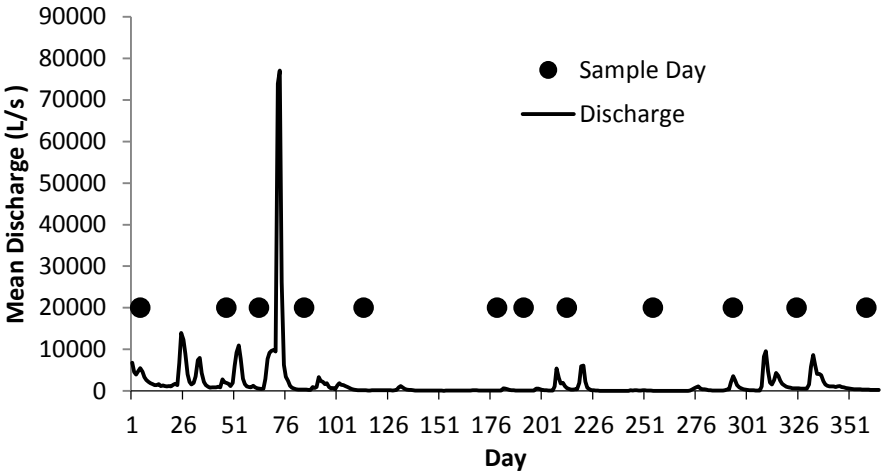


Figure 16. Average discharge each day at the White Oak Creek gauge and days sampled throughout the study period.

Two models were used to estimate daily and annual load and export of the chemical constituents in WOCMS2 the gauged site on the main stem. For some concentrations there was a strong negative of positive relationship between natural log concentration and natural log discharge but for others no relationship between concentration and discharge was found (Table 3).

Ammonium-N, fluoride, sulfate and DOC produced a stronger relationship with discharge when the concentration was untransformed. Overall only nitrate-N, alkalinity, and TDN had a reasonable relationship with discharge; of those nitrate-N and TDN were positively related to discharge and alkalinity negatively related to discharge. To remedy

this I also examined linear interpolation to estimate the concentrations of each chemical constituent on the days not sampled.

Table 3. Slopes, coefficients and R^2 for the Ln-Ln model to determine concentrations on days not sampled. Significant relationships * $\alpha < 0.05$ and ** $\alpha < 0.01$.

Constituent	Concentration	Discharge	Slope	Coefficient	R^2
Ammonium-N	mg/L	Ln L/sec	0.0129	0.0391	0.27
Nitrate-N	Ln mg/L	Ln L/sec	0.4	3.209	0.39*
Phosphate-P	Ln mg/L	Ln L/sec	0.1895	3.6516	0.15
Alkalinity	Ln mg/L	Ln L/sec	-0.2116	5.4072	0.57**
Sodium	Ln mg/L	Ln L/sec	-0.1611	4.6052	0.31
Potassium	Ln mg/L	Ln L/sec	0.0072	1.9144	0.0055
Magnesium	Ln mg/L	Ln L/sec	0.028	1.7915	0.02
Calcium	Ln mg/L	Ln L/sec	0.0393	2.5638	0.031
Fluoride	mg/L	Ln L/sec	-0.0285	0.403	0.114
Sulfate	mg/L	Ln L/sec	-9.0963	116.24	0.144
Chloride	Ln mg/L	Ln L/sec	-0.0587	3.854	0.0687
DOC	mg/L	Ln L/sec	0.7488	5.2265	0.16
TDN	Ln mg/L	Ln L/sec	0.202	1.19	0.54**

Annual load and export for each of the chemical constituents was calculated using the LI model and Ln-Ln model for comparative purposes (Table 4). Seven metric tonnes of ammonium-N went through the White Oak Creek gage which corresponds to an export of 4.7 kg km^{-2} yr^{-1}. Nitrate-N load and export was greater than that of ammonium-N at 85 metric tonnes corresponding to 54.4 kg km^{-2} yr^{-1} (Table 4). Of the cations, sodium was dominant with a load of 1933 metric tonnes and an export of 1241 kg km^{-2} yr^{-1}. Sulfate was the dominant anion with a load of 1998 metric tonnes and export of 1283 kg km^{-2} yr^{-1}.

Dissolved organic carbon losses from a watershed correspond to losses of terrestrial carbon. At White Oak Creek 578 metric tonnes were lost during the study period representing an export of 371 kg km^{-2} yr^{-1}. Dissolved organic nitrogen annual load was 17.5 metric tonnes with an export of 27 kg km^{-2} yr^{-1}. Thus nitrate-N was the dominant nitrogen species released from this watershed. Of the other nutrients, Orthophosphate-P had an annual load of 5 metric tonnes and an export of 3.2 kg km^{-2} yr^{-1}.

Table 4. Estimated concentrations, annual load and export of chemical constituents at the White Oak Creek gauge. The LI model represents linear interpolation between observed concentrations and the Ln-Ln model regression analysis between Ln discharge and transformed or Ln transformed concentrations. Values in bold represent those concentrations and exports that are used in comparison with other studies.

	LI Model			Ln-Ln Model		
Chemical	Mean Concentration mg/L	Annual Load tonne/yr	Export kg/km^2/yr	Mean Concentration mg/L	Annual Load tonne/yr	Export kg/km^2/yr
Ammonium-N	**0.12**	**7**	**4.7**	0.12	9	5.6
Nitrate-N	0.57	45	28.8	**0.57**	**85**	**54.4**
Phosphate-P	**0.11**	**5**	**3.17**	0.09	8	5.32
Alkalinity	64.55	3124	2010	**64.46**	**2043**	**1312**
Sodium	**38.95**	**1930**	**1241**	38.50	1398	898
Potassium	**7.30**	**405**	**260**	7.30	420	270
Magnesium	**7.15**	**443**	**285**	7.13	435	279
Calcium	**16.88**	**1014**	**651**	16.55	1042	669
Fluoride	**0.22**	**12**	**8**	1.26	66	42
Chloride	**32.85**	**1892**	**1215**	33.08	1588	1020
Sulfate	**57.41**	**2984**	**1916**	60.54	1998	1283
DOC	**9.66**	**578**	**371**	9.81	671	431
TDN	1.05	77	49	**1.11**	**109**	**70**
DON	**0.43**	**27**	**17**	0.42	16	10
TSS	**56.58**	**2407**	**1546**	35.09	2773	1781

3.4 Land Use and Land Management Effects on Surface Water Chemistry

For an initial examination of possible land use interaction with sub-catchment surface water chemistry I performed a Pearson bivariate correlation analysis. All sub-catchment classified land uses were correlated so some surface water chemistry with the exception of wetlands. Open water in a sub-catchment such as reservoir or lake was negatively correlated with surface water electrical conductivity ($R = -0.56$; $p = 0.03$), calcium ($R = -0.59$; $p = 0.02$) and chloride ($R = -0.59$; $p = 0.02$) as such that if an open water source was in the catchment then these surface water chemical constituents decreased in the surface waters (Table 5). Urban open areas in a sub-catchment were positively correlated with conductivity ($R = 0.71$; $p < 0.001$), ammonium-N ($R = 0.60$; $p = 0.02$) and calcium ($R = 0.66$; $p = 0.01$). Low, medium and high density urban development was positively correlated with surface water conductivity ($R = 0.74$-0.79; $p < 0.01$), ammonium-N ($R = 0.77$-0.79; $p < 0.01$), calcium ($R = 0.77$-0.81; $p < 0.01$) and dissolved organic carbon ($R = 0.60$-0.62; $p < 0.05$). A correlation between magnesium and urban land use only occurred in the medium and high-density land use ($R = 0.53$-0.56; $p <0.05$) and was not as strongly correlated as the other chemical constituents (Table 5). Dissolved organic nitrogen had a negative relationship with barren land as such that as barren land in a watershed increased then DON in surface water decreased (Table 5).

Agricultural land use also had effects on surface water chemistry (Table 5). Moderate, positive correlations were found between pasture and soluble phosphate-P ($R = 0.52$; $p < 0.05$), DON ($R = 0.67$; $p = 0.01$), total suspended solids ($R = 0.66$; $p = 0.01$)

and turbidity (0.66; $p = 0.01$) and negative correlation with the DON:TDN ratio ($R = 0.52$; $p < 0.05$). Agricultural cropland was also correlated to some chemical constituents found in surface waters across the sub-catchment dataset. Interestingly as the proportion of cropland in a sub-catchment increased so did dissolved oxygen in surface waters ($R = 0.56$; $p < 0.05$). Other correlations between the proportion of agricultural crop in a sub-catchment and surface water chemistry were negative; for example, pH ($R = -0.61$; $p = 0.01$), alkalinity ($R = -66$; $p = 0.01$), fluoride ($R = -0.73$; $p < 0.01$) and the DON:TDN ratio ($R = -0.66$; $p = 0.01$).

Natural resource land use such as forestry had differing correlations with sub-catchment surface water chemistry (Table 5). Deciduous forests were negatively correlated with surface water nitrate-N ($R = -0.54$; $p < 0.05$), soluble phosphate-P ($R = -0.55$; $p < 0.05$), sulfate ($R = -0.54$; $p < 0.05$), DOC ($R = -0.63$; $p = 0.01$) and BOD_5 ($R = -0.52$; $p < 0.05$). The proportion of evergreen forests in a sub-catchment appeared to have a different effect on surface water chemistry relative to deciduous forests. Although there was a similar response in surface water sulfate ($R = -0.69$; $p < 0.01$) and DOC ($R = -0.51$; $p <0.05$), evergreen forest had a positive influence on surface water chloride ($R = 0.53$; $p <0.05$) and negative correlations were found for TSS ($R = -0.57$; $p<0.05$) and turbidity ($R = -0.57$; $p<0.05$). There we no negative or positive correlations between surface water chemistry and mixed forests. Rangeland, shrub and scrub was positively correlated with the DON:TDN ratio ($R = 0.56$; $p<0.05$) and negatively correlated with TSS ($R = -0.57$; $p< 0.05$) and turbidity ($R = -0.57$; $p<0.05$).

Table 5. Pearson bivariate correlation between sub-catchment surface water chemistry and land use. *Significant at $\alpha < 0.05$ and **significant at $\alpha < 0.01$.

		URBAN									AGRICULTURE	
	water	Open	Low	Medium	High	Barren	Deciduous	Evergreen	Mixed	Range	Pasture	Crop
pH	-0.35	-0.15	-0.01	-0.05	-0.05	-0.16	0.23	0.38	0.52	-0.03	0.01	-0.61**
EC	-0.56*	0.71**	0.79**	0.74**	0.74**	-0.21	-0.25	-0.34	-0.11	-0.10	-0.16	-0.28
NH_4—N	-0.27	0.60*	0.77**	0.79**	0.78**	0.05	-0.46	-0.28	-0.07	-0.10	-0.25	-0.23
NO_3-N	-0.17	0.15	0.26	0.28	0.27	-0.21	-0.55*	-0.45	-0.16	-0.29	0.21	0.10
PO_4-P	0.00	0.16	0.17	0.15	0.15	-0.33	-0.55*	-0.50	-0.06	-0.46	0.52*	0.00
Alkalinity	-0.18	-0.15	-0.03	-0.04	-0.06	-0.07	0.24	0.39	0.44	0.07	-0.04	-0.66**
Mg^{2+}	-0.50	0.42	0.58	0.53*	0.53*	-0.27	-0.16	0.10	0.18	-0.33	-0.02	-0.43
Ca^{2+}	-0.59*	0.66**	0.77**	0.80**	0.81**	-0.37	-0.34	-0.24	0.02	-0.45	-0.09	-0.09
F^-	-0.05	-0.22	-0.08	-0.13	-0.13	-0.08	0.47	0.36	0.43	0.22	-0.14	-0.73**
Cl^-	-0.59*	-0.04	0.03	0.01	0.00	0.04	0.11	0.53*	0.32	-0.16	0.05	-0.31
SO_4^{2-}	-0.26	-0.04	-0.08	-0.16	-0.15	-0.46	-0.54*	-0.69**	-0.40	-0.17	0.49	0.28
DOC	-0.20	0.47	0.62**	0.60*	0.60*	-0.20	-0.63**	-0.51*	-0.15	-0.22	0.04	-0.09
DON	-0.21	-0.22	-0.38	-0.45	-0.43	-0.56*	-0.24	-0.37	-0.28	-0.40	0.67**	0.37
DONTDN	0.02	-0.24	-0.06	-0.05	-0.07	0.34	0.42	0.45	0.26	0.56*	-0.52*	-0.66**
DO	-0.27	0.03	-0.09	-0.03	-0.03	-0.15	-0.42	-0.26	-0.28	-0.38	0.40	0.56*
BOD	0.20	0.33	0.39	0.36	0.36	-0.29	-0.52*	-0.30	-0.13	-0.53*	0.47	0.13
TS	-0.33	0.35	0.40	0.37	0.37	-0.27	-0.51	-0.30	-0.14	-0.54*	0.47	0.16
TSS	-0.24	-0.20	-0.27	-0.27	-0.28	-0.34	-0.51	-0.57*	-0.23	-0.34	0.66**	0.20
Turbidity	0.09	1.00	-0.27	-0.27	-0.28	-0.34	-0.51	-0.57*	-0.23	-0.34	0.66**	0.20

4. DISCUSSION

Relatively little research is published on general stream water chemistry in sub-tropical and semi-arid ecosystems (Mulholland and Watts 1982; Figueiredo and Ovalle 1998; Yuan et al. 2007; Aitkenhead-Peterson et al. 2011; Slye et al. 2011; Steele and Aitkenhead-Peterson 2011) relative to stream water chemistry in temperate ecosystems. Furthermore, surface water chemistry is researched more frequently in temperate and tropical forested (e.g. Ertel et al. 1986), temperate peatland (e.g. Aitkenhead et al. 1999; Kortelainen et al. 1997) and urban watersheds (e.g. Sickman et al. 2007; Petrone 2010; Aitkenhead-Peterson et al. 2011; Mouri et al. 2011) than in mediterranean or sub-tropical rangeland ecosystems (Lewis et al. 2007; O'Green et al. 2010). Thus the relative effect of land use and land management practices on stream chemistry in sub-tropical rangeland ecosystems, where much of the land use is converted to pasture and agriculture is largely unknown. One of the major objectives of my research was to determine the cause of low dissolved oxygen in White Oak Creek, a tributary of the Sulphur River in North-East Texas

4.1 Concentrations of Chemical Constituents in White Oak Creek Sub-catchments

4.1.1 Dissolved Oxygen

Dissolved oxygen (DO) is a recorded impairment on the TCEQ 303d list in White Oak Creek. I expected to find that high nutrient inputs such as nitrogen and phosphorus and high total suspended solids would be a causative factor affecting low DO concentrations. Dissolved oxygen in the main stem and sub-catchments of White

Oak Creek during my twelve sampling campaigns throughout 2010 and 2011 yielded DO concentrations that averaged from 7.3±1.4 to 8.3±0.4 mg/L among the 15 sub-catchment sample sites which was much higher on average than that recorded by TCEQ whose data ranged from 3.1 to 11.6 mg/L and averaged 6.36 mg/L during 2010. The first year that White Oak Creek was listed on the 303d list in 2000 for depressed dissolved oxygen, DO data ranged from 3.8 to 10.4 mg/L, with mean concentration of 6.03 mg/L (TCEQ 2010a). To examine why my DO readings were higher than those reported by TCEQ I decided to conduct a 12h and a 24 h monitoring of DO using the same protocol used by TCEQ (Table 6). It was likely that my collection of samples may have been during a part of the day that DO normally peaked in streams (Goldman and Horne 1983) or that the method I was using to quantify DO was compromised by the long travel time between stream water collection and measurement of DO.

Table 6. Dissolved oxygen concentration and percent in White Oak Creek during spring 2011.

12 Hour				24 Hour			
Time	DO (mg/L)	DO %	Temp °C	Time	DO (mg/L)	DO %	Temp °C
0700	5.37	56	17.7	0630	5.23	57.9	20.3
0800	5.39	56.6	17.7	0830	5.23	58	21.2
0900	5.42	57.7	18.1	1030	5.21	58.7	21.2
1000	5.4	57.5	18.3	1230	5.28	60.1	21.8
1100	5.55	59.6	18.6	1430	5.47	62.8	22.1
1200	5.49	59.1	18.8	1630	5.23	60.1	22.2
1300	5.52	59.4	19.2	1830	5.34	62.2	22.2
1400	5.57	61	19.7	2030	5.43	60.9	21.6
1500	5.55	60.8	19.7	2230	5.45	61	20.9
1600	5.53	60.5	19.7	0030	5.48	61.1	20.6
1700	5.54	60.5	19.6	0230	5.49	61	20.6
1800	5.55	60.8	19.6	0430	5.33	59.1	20.4

The measurements for DO were taken at WOCMS2 site on the main stem. The 12 h dissolved oxygen measurements taken after a storm event showed very little fluctuation with a minimum of 5.37 mg/L in the morning and maximum 5.57 mg/L mid-afternoon. Twenty-four hour DO have similar concentrations ranging from 5.21 to 5.47 mg/L. Measurement for the 24 h DO was taken after a period of no rainfall. Although my mean annual DO concentrations among the sites I sampled was higher than that reported by TCEQ, my average DO concentrations taken in the spring at WOCMS2 using TCEQ protocol were lower, although concentrations were still above the 4.0 mg/L minimum standard designated by TCEQ.

Some characteristics of a watershed and its stream are known to depress DO. For example higher temperatures typically reduce the concentration of DO in water (Goldman and Horne 1983); higher salinity, or salt content also depress DO concentrations in surface water (Goldman and Horne 1983; Kim et al 2010). Finally, elevation or atmospheric pressure has an impact on DO concentrations in surface waters with higher elevations experiencing lower DO concentrations, and lower elevations experiencing higher DO concentrations (Goldman and Horne 1983). Water flow in the channel as turbulent or laminar flow, presence or absence of aquatic vegetation, and bacterial and nutrient loading have also been shown to affect surface water DO concentrations and increase CO_2 concentrations (Goldman and Horne 1983; Kim et al 2010). In my study, alkalinity was inversely correlated with DO concentrations in the sub-catchments but the correlation was very weak though significant. This would make some sense because alkalinity is a measure of calcium carbonate and a form of dissolved

inorganic carbon (DIC). Form of DIC depends upon the pH of the surface water, with low pH having DIC in the form of CO_2, moderate pH having DIC in the form of HCO_3^-, and high pH having DIC in the form of HCO_3^{2-} (Cole 1994). Typically DO is consumed by aquatic microorganisms or fauna and hence CO_2 released. The data also showed a moderate positive correlation between DO and cultivated cropland, suggesting that as crop area increased DO concentrations increased. This data is contrary to what I had predicted, as typically fertilizer application to cropland might result in a decrease in DO concentrations (Goolsby et al. 2001) if those nutrients are transported to streams.

Based on my results, dissolved oxygen concentrations in White Oak Creek and its sub-catchments did not indicate a serious concern to water quality. Hypoxic conditions exist at DO concentrations below 2 to 3 mg/L (USEPA 2010), much lower than that measured during my sampling campaigns. No clear correlation between DO and land use or any other chemical constituent in the study is likely due to very little fluctuation in DO concentrations among the sub-catchments throughout the sampling period.

My findings found no land use or land management effect on mean annual concentrations and I found no cause for concern relating to DO concentrations in White Oak Creek. However the differences between returning the sample to the laboratory (5 – 24 hours) prior to measuring DO and measurement in stream on site was large suggesting that in retrospect DO concentrations should be measured and recorded *in situ*.

4.1.2 Inorganic Nitrogen and Phosphorus Concentrations

Inputs of nitrogen and phosphorus to waterways can result in impairments and potential eutrophication not only at the local scale, but also through accumulation or addition of loading at points further downstream (Goolsby et al 2001; Kemp et al 2005). Continuous and sustained contributions of nitrogen and phosphorus, we now understand, can have very significant environmental impacts to large bodies of water such as those observed in the Chesapeake Bay, and the Gulf of Mexico (Goolsby et al 2001; Kemp et al 2005; Osterman et al 2009; Brush 2009). Therefore identifying sources of nitrogen and phosphorus in watersheds that eventually make their way to surface waters and these near coastal zones is crucial for directing upstream management.

Inputs from fertilizer contribute ammonium ions (NH_4^+) to the soil that can be leached into the groundwater if not converted to NO_3^- or adsorbed to the negative charge on clay particles and transported to streams on eroded soils (Donstova et al 2005). Volatilization of ammonium is also a problem in agricultural watersheds (Jarvis and Pain 1990). Ammonium also accounts for approximately half of the nitrogen content of manure. Jokela and Meisinger (2008) and Houlbrooke et al. (2004) reported that manure from farm dairy effluent can be a major source of total nitrogen to surrounding surface waters of pastured land. Ammonium ions are also commonly found in urban runoff transported to streams (Brainwood et al. 2004) and wastewater effluent discharged into rivers (Brion and Billen 2000).

In the sub-catchments studied in White Oak Creek Watershed, urban runoff, wastewater effluent, and manure are all likely contributors of ammonium-N.

Characteristic of what has been observed in urban watersheds, sub-catchment WOCT2 had the highest ammonium-N concentrations (mean 0.32 mg/L) and also the highest percentage of urban development (52%) of the sub-catchments examined. Furthermore I found that between 74 and 79% of the variance in ammonium-N among my sub-catchments was described by urban development. Ammonium-N inputs associated with urban development was also observed by Brainwood et al., (2004) in New South Wales, Australia where ammonium ions found in farm dams with adjacent urban development were a contribution of urban runoff. Contributions of ammonium-N from cattle manure are also likely in Lewis and WOCT8, which also had significantly higher annual mean ammonium-N concentrations because of the higher proportion of improved pasture in their watersheds.

Nitrate-N is a highly soluble and mobile form of nitrogen and can easily be leached into the groundwater and streams (Malhi et al. 2011). High nitrate-N concentrations in surface waters are generally associated with high population density and development, and row crop agriculture (Goolsby et al. 2001). In my study, nitrate-N was not significantly correlated with agricultural crops or urban development but WOCT2, with the highest proportion of urban development had the highest mean annual concentration of nitrate-N. Deciduous forests were negatively correlated with nitrate-N in my study, supporting the findings of Daniel et al. (2009) in the Little Miami River Basin, a tributary of the Ohio River. Those sub-catchments with the lowest nitrate-N concentrations (WOCT6, WOCT13, Ripley, Piney and Lewis) all had a relatively high proportion of deciduous forest land cover ranging from 14 to 30 percent in their

watersheds. This suggests that the land management practice of leaving some deciduous forest, particularly if used as a buffer between the stream and urban and agricultural land uses may reduce nitrate-N movement to surface waters. However, during timber harvest a combination of soil aeration which leads to nitrification and removal of vegetation that would normally take up nitrate results in enhanced streamwater nitrate concentrations (Hornbeck et al. 1986). Increases in stream nitrate-N exports were observed for the three years after timber harvest only (Hornbeck et al. 1986) which suggests that as ground cover increased, plant uptake of nitrate-N also increased. Mean annual nitrate-N concentrations in the White Oak Watershed sub-catchments were comparative to forest and urban land uses reported in a study in the Kalamazoo River Basin in Michigan, USA where mean nitrate-N concentrations for forested watersheds ranged from 0.01 mg/L to 0.4 mg/L and urban watersheds ranged from 0.2 mg/L to 1.1 mg/L (Johnson et al. 2009). Mean annual nitrate-N concentrations in Kalamazoo watersheds dominated by agriculture were much higher than I found in the White Oak Creek sub-catchments where they ranged from 0.3 mg/L to 17.5 mg/L (Johnson et al. 2009) compared to 0.13 mg/L to 0.97 mg/L in my sub-catchments. Differences in type of agricultural watersheds can help to explain the lower nitrate concentrations found in my study. Johnson et al.'s (2009) study focused on row crop agriculture, while my study based agricultural activity on pastured farm land, where nitrogen inputs are likely to be less intense. Another reason for lower nitrate in my streams may be stream length differences. Longer streams have the potential to denitrify nitrate resulting in lower concentrations downstream. Sub-catchment WOCT9 has the highest proportion of wetland in its watershed yet it had

relatively high nitrate concentrations. Mitsch et al. (2005) showed that wetlands can act as a beneficial sink for nitrate-N, which can be retained in wetland areas which can be used as a buffer zone to reduce agricultural impacts to downstream loading. Because wetlands are water saturated and therefore anaerobic, nitrate-N is reduced and released into the atmosphere as nitrous oxide. Why my subcatchment with the highest proportion of wetland did not have significantly lower nitrate-N concentration in its stream is unknown.

Manure from cattle on dairy farms and ranches are also an important source of nitrate-N to the soil in the watershed. Studies have shown that nitrate-N content of the total nitrogen found in dairy manure can vary depending on the type of feed or vegetation consumed by the cattle (Tomlinson et al. 1996; Chastain and Camberato 2004). Dairy manure from South Carolina has been reported to contain between 0.02 mg/L to 0.1 mg/L NO_3^- (Chastain and Camberato 2004) which has the potential to be transported into adjacent streams or directly deposited into the stream by cattle keeping cool or drinking water (Belsky et al. 1999). Contributions from two permitted dairy farm discharges, as well as other cattle in the watershed may be the cause of relatively high nitrate-N concentrations in WOCT7 sub-catchment.

Discharge and nitrate-N on the main stem of White Oak had a significant positive relationship (Table 3). This suggests that nitrate-N concentrations increase in response to storm events and that the hydrological flowpath is likely throughflow through the upper organic soil horizons or Hortonion overland flow leaching and transporting nitrate-N to the stream. Additional sources of nitrate-N in a watershed

may be due to application of fertilizers for hay production (Randall et al. 1997). Here nitrogen is stored in the soil as a result of dry conditions when crop uptake is reduced; nitrate is then flushed out during wetter periods at above normal concentrations. This scenario was unlikely to have occurred in my sub-catchments because of the relatively constant precipitation events during my sampling year though may have contributed to the nitrate-N during the drier period in late summer. Over application of fertilizers can also lead to a build-up of nitrate-N in the soil where higher concentrations could be flushed during one storm event.

Phosphorus loss to waters from surface runoff and subsurface flow has also been related to land management practices and soil properties (Sharpley et al. 2007). Sub-catchment WOCT7 had the highest annual mean concentration of PO_4-P (0.44 mg/L). During my sampling year this site was undergoing a significant amount of clear-cutting for timber harvest. Undisturbed watersheds typically have low PO_4^{3-} concentrations as a study on undeveloped stream basins in the U.S revealed; where maximum PO_4^{3} concentrations did not exceed 0.13 mg/L (Clarke et al. 2000). Timber harvesting activities can alter watersheds and initiate erosion processes. Subsequent runoff from disturbed and exposed soils may contain phosphorus-bound soil particles resulting in higher concentrations of soluble phosphate-P reaching the stream. Soluble phosphate exhibits a very strong negative charge and will typically bind tightly to mineral soil adsorption sites (McDowell et al. 2001). The main path of transport for these particles to streams is by overland flow. McDowell et al. (2001) showed that during storm events in a tributary of the Susquehanna River, overland flow can originate from as far as 62 m

away from the stream channel; however 90% of overland flow occurs within 30 m of the stream channel.

Higher nitrate-N concentrations coupled with higher soluble phosphate-P concentrations at WOCT 7 may also be indicative of farm dairy discharge into the tributaries of this watershed as mentioned above. The positive correlation between PO_4-P and pasture in my study was consistent with a study conducted in Red Hill State Forest, Australia which compared pasture and forest catchments (Vink et al. 2007). Vink et al. (2007) reported that mean PO_4-P concentrations were higher in the pasture catchment relative to the forested catchment. A similar observation was reported in Dorset, U.K. where orthophosphate was most dominant in pasture soils compared to cultivated soils (Ballantine et al. 2009). Further, research conducted on nutrient delivery to surface waters from dairy farms showed that surface applications of manures resulted in temporary increases in water soluble P at the soil surface, and therefore increased the likelihood of elevated concentrations of soluble P in surface runoff (Knowlton et al. 2006). The combination of increasing areas of exposed soil from timber harvest disruption, as well as significant percentages of pastured land in the watershed could explain the elevated concentrations of orthophosphate in sub-catchment WOCT7.

Sources of phosphorous in urban watersheds include wastewater effluent and fertilizers (LaValle 1975). LaValle (1975) assessed the relationship between stream orthophosphate and domestic sources and found that 76% of the variation in stream PO_4^{3-} concentrations was accounted for by the percentage of households connected to the municipal sewer system. Sub-catchment WOCT2 with the highest percent of urban

development was one of the catchments that had significantly higher PO_4^{3-} concentrations with mean 0.2 mg/L and maximum 0.44 mg/L. Panno et al. (2007) took effluent samples from the discharge pipes of on-site residential septic systems in Illinois and found PO_4^{3-} concentrations ranging from 1.4 to 48 mg/L with mean 9.31 mg/L. The range reported by Panno et al. (2007) is well above that observed in the White Oak Creek sub-catchments, but can be recognized as a potential source of PO_4^{3-} to streams in the subcatchment if septic systems are located in close proximity to stream channels. Sewage effluent from moderate urban development was also attributed to higher phosphate concentrations ranging from 0.05 mg/L to 0.7 mg/L, in a study by Robson and Neal (1997) in a rural U.K. catchment. Robson and Neal (1997) results are comparative to what was observed in WOCT2 with no direct municipal wastewater discharge.

4.1.3 Cation Concentrations

Cations in surface waters are typically higher under baseflow conditions reflecting the underlying geology of the watershed (Billett et al. 1996). Bedrock has been found to largely influence the presence and load of cations in Texas groundwater (Hudak 1999). Hudak (1999) reported that sodium concentrations are naturally relatively low in northeast Texas groundwater, with sodium ranging from 21 to 100 mg/L in northeast Texas counties. Low flow conditions as a result of lack of major storm events during the late summer months of the sampling period resulted in sodium concentrations ranging from 11.1 to 81.3 mg/L with a mean dry period concentration of 34.0 mg/L (calculated from sample days 5,6,7, and 9) throughout the fifteen sub-catchments. These sodium concentrations reflect concentrations observed in groundwater in this area by

Hudak (1999). Additional contributions of sodium have also been identified in reclaimed wastewater effluent (Provin and Pitt 2002). The Mt. Vernon water treatment facility in WOCT8 uses NaOH (caustic soda) as a treatment chemical for potable water, thus higher concentrations of sodium in municipal water that reaches the wastewater treatment plant upstream of the sampling point at WOCT8 may explain the elevated concentrations of sodium relative to the other sub-catchments. Other factors such as diets high in sodium consumption, laundry detergents containing sodium, and the addition of sodium hydroxide for potable water treatment are all being recognized as contributing to high sodium in effluent discharge (Steele and Aitkenhead-Peterson 2011; Steele et al. 2010).

N-P-K fertilizer is commonly applied in northeast Texas due to the high volume of hay production and pasture management for grazing animals (Northeast Texas Farmers COOP 2011). Fifty-five percent of the land in WOCT7 is used for pasture and hay production for dairy farming. Inputs of potassium into the adjacent streams resulting from fertilizer application was also observed at Muddy Creek outside of Harrisburg, VA where K^+ concentrations after application and following a storm event increased 5-fold at two different sites from <5 mg/L to 25 mg/L and from 10 mg/L to 50 mg/L via overland flow (Hyer et al. 2001). Chen and Driscoll (2009) also reported higher K^+ concentrations in an agricultural watershed (range 2.5 mg/L to 16 mg/L), which was similar to the concentrations at WOCT7. Chen and Driscoll (2009) concluded that the higher concentrations found in their study were likely due to the combination of fertilizers, manure application, mineralization of organic matter and weathering.

Another possible contribution of potassium to streams in this particular watershed may be a result of the timber harvesting that was occurring during the sampling period. The Hubbard Brook experiment also provides insight into processes of timber harvest and potential impacts to surface water quality. Potassium concentrations tripled from 0.3 mg/L to 0.9 mg/L, and peaked at 1.25 mg/L immediately following whole tree harvest at the Hubbard Brook experimental forest in New Hampshire (Hornbeck and Federer 1975). Potassium concentrations remained elevated in the following 20 years since the initial clear cut. Because potassium is rarely seen in high concentrations in forested watershed streams, this suggests that a prime sink for postassium is plant uptake. Potassium concentrations are exceedingly high in throughfall and vegetation in forested watersheds (Likens et al. 1994) and removal of vegetation through timber harvest will result in potassium available for runoff.

Inputs of potassium to sub-catchment WOCT8, which also had high mean annual concentrations of potassium were likely due to direct inputs of potassium alum [$KAl(SO_4)_2$ $12H_2O$] at the Water Treatment Plant. Potassium alum is commonly used as a flocculating agent in the water purification process to remove negatively charged colloids (Lenntech 2011). Potassium and sulfate dissolve in the water and the aluminum ion adsorbs the colloids for removal. Potassium and sulfate are subsequently cycled through the system to the wastewater treatment plant.

Calcium and Magnesium are abundant in natural waters due to the weathering of rocks such as limestone ($CaCO_3$), dolomite ($[CaCO_3]_2$ and $[MgCO_3]_2$), and minerals such as calcite and magnesite ($CaCO_3$ and $MgCO_3$). Mean annual concentrations of

calcium and magnesium were positively correlated with urban development, particularly medium and high-density development. Sub-catchment WOCT2 had the highest proportion of its watershed under urban development and further had an annual mean concentration of 26.48 mg/L of calcium, which was much higher than that recorded in Brazil on research studying land use effects on benthic communities (Hepp and Santos 2008). In the Hepp and Santos (2008) study a catchment located in an urban watershed was measured having calcium concentrations of 8.0 mg/L. The contribution from bedrock geology in the White Oak Creek watershed can help account for elevated concentrations of calcium. Approximately forty-four percent of this sub-catchment is underlain by a fine-grained mixed clastic and limestone formation. Urbanization has been shown to increase some surface water base cations and decrease others (Steele et al. 2010). For example as urbanization increases surface water calcium and magnesium decrease and sodium and potassium increase (Steele et al. 2010). There is little contribution from sewage effluent to calcium and magnesium concentrations in surface waters (Steele et al. 2010) and so contributions of calcium and magnesium in an urban watershed may include road dusts, deicing salts and horticultural products. Therefore, calcium and magnesium inputs may largely be attributed to geologic formations and weathering in my subcatchments. Data in the White Oak Creek Watershed for $CaCO_3$, is generally much higher than the data gathered by Hudak (1999) for northeast Texas on geologic contributions. Their research found that regional $CaCO_3$ concentrations for the area ranged from 0 to 60 mg/L, yet mean annual concentration of $CaCO_3$ for sub-catchment WOCT7 exceeded this at 104.8 mg/L. Only one-third of the mean annual

surface water $CaCO_3$ concentrations for White Oak Creek sub-catchments are below 60 mg/L $CaCO_3$, with the lowest mean concentration of 36.9 mg/L.

4.1.4 Anion Concentrations

Twenty-four percent of the variation in surface water chloride concentrations is explained by urbanization (Steele et al. 2010). Chloride is typically correlated with sodium and is a measure of overall salinity. Sodium and chloride are naturally occurring constituents of surface waters with sources including geological weathering, marine aerosols, salt water intrusion and atmospheric deposition (Steele et al. 2010). High concentrations of chloride in surface waters can have a detrimental effect on aquatic fauna. Enrichment of chloride in surface waters has been reported in northern states as a result of long-term application of de-icing salts (Kaushal et al. 2005) but recent research on the Trinity River in Texas, USA reported that chloride loading and exports were similar to those reported from northern watersheds even though the use of deicing salts was minimal in Texas (Steele and Aitkenhead-Peterson 2011). Greater chloride contributions are more commonly observed in the northeast U.S. where road salt application runs off into nearby waterways or in areas of greater urban or suburban development (Kaushal et al. 2005; Daley et al. 2009). Elevated chloride concentrations in a forested catchment were also observed in a rural watershed in Eastern New York throughout the entire year, not strictly during winter road salt application periods and concentrations ranged from 16.6 mg/L to 104.7 mg/L at two different tributaries (Madden et al. 2007). Research conducted in Oklahoma, with similar geographic and land use characteristics as my study sought to determine potential sources of chloride to

surface and ground waters where it was determined that sources were likely anthropogenic coming from septic waste, wastewater treatment plant effluent, industrial waste, animal waste, fertilizer, and produced water from oilfield operations (Mashburn and Sughru 2004). Highest mean annual concentration of chloride (53±16 mg/L) was found in WOCT8, which had the City of Mt. Vernon's waste water treatment facility in its headwaters. Drinking water in this sub-catchment is pre-treated with chloride, likely contributing to the elevated concentrations of Cl^- found in the tributary. Even so, relatively high mean annual concentrations of chloride were found in sub-catchments without wastewater facilities. These catchments, WOCT6, WOCT7, WOCT14, WOCT13, Ripley, Piney, and Lewis (33±8 to 49±16 mg/L) all had forest land cover ranging from 14 to 42 percent. It is difficult to determine exact sources of chloride within these watersheds. Possible contributions may be from septic systems leaching chloride derived from household cleaning products to the groundwater and into the stream. Other research has shown that forests may act as a sink for chloride, and retention and release may be depend on the availability of oxygen or organic matter present (Bastviken et al. 2006). The exact conditions for chloride retention are still unclear, having a single negative charge it was assumed chloride to be a conservative ion and it was commonly used as a tracer in the past. Nevertheless, the surface water concentrations of chloride in White Oak Creek sub-catchments are much lower than those reported for many watersheds.

Natural contributions of fluoride in the watershed can be a result of rock weathering and is typically higher in concentration in granitic aquifers (Arveti et al.

2011). Fluoride concentrations in groundwater wells in India where excess fluoride is linked to detriments in human health ranged from 0.78 to 5.40 mg/L, much higher than the range found in White Oak Creek sub-catchments (0.09±0.06 to 0.4±0.3 mg/L) reflecting the difference in bedrock geology. Anthropogenic inputs can also be accredited to fertilizer runoff and industrial activities. Fluoride's negative correlation with cultivated crop activities in the tributaries of White Oak Creek infers that fertilizer may not be a contributing factor to surface water quality for this particular ion. The most urbanized sub-catchment (WOCT2) had significantly higher fluoride concentrations than the other catchments, and although there is not a wastewater treatment facility in this catchment, fluoride is added to the city of Sulphur Spring's drinking water supply at a rate of 0.7 mg/L (Mount Vernon Water Treatment 2011). Therefore, it is likely that fluoride may be released through subsequent pathways into the groundwater or stream system from lawn irrigation, septic systems, or urban runoff. Previous chemical additions to drinking water supply were seen in sub-catchment WOCT8, whereas fluoride concentrations are not elevated in this tributary, largely as a result of fluoride not being added to this area's drinking water supply.

Higher sulfate concentrations in surface waters are typically observed in watersheds with mining activities (Davies et al. 2011) and in watersheds where the underlying geology contains iron pyrite which is exposed through weathering or road cuts (Reinhardt 1999). High sulfate concentrations were also observed in watersheds subjected to sulfur deposition during the acid rain era (Norton et al. 1988), and watersheds impacted by volcanic eruptions (Ezoe et al. 2002). While sulfate shows a

pattern of increase with urbanization it is not a strong relationship (Steele et al. 2010). Previous and ongoing lignite coal surface mining activities in the area are located in the south-eastern portion of the watershed. The primary composition of coal is carbon with secondary composites of sulfur, hydrogen, oxygen, and nitrogen. Overall pH for the entire watershed and particularly those sub-catchments (WOCT8, WOCT13, Ripley, and Piney) with high sulfate concentrations are well within the acceptable range of pH values, therefore acidic mine drainage is not a factor in this study. Both Ripley and Piney sub-catchment headwaters are directly located in what is now reclaimed mine land. Sub-catchment WOCT13 has the second highest percentage of coal formation out of the sub-catchments and WOCT8 sub-catchments headwaters are largely dominated by coal formation. Therefore, higher sulfate concentrations may largely be a result of rock weathering from iron pyrite minerals. Seventy-three percent of the variance in sulfate was explained by sodium in my sub-catchments ($R^2 = 0.73$; $p < 0.01$); sodium sulfate occurs naturally from mineral deposits and is likely to be responsible for sulfate concentrations in my streams, furthermore it should be noted that the higher surface water sulfate concentrations occurred in a region underlain by clastic/coal deposits (Figure 2) which likely was the driver of high sulfate. Highest mean annual sulfate concentrations from surface waters in reclaimed surface mine land in my watershed were lower than those concentrations reported by Helsel (1983) in reclaimed surface mine land in Ohio surface waters where concentrations ranged from 301 to 659 mg/L as compared to mean concentrations at Piney at 104.4±44.4 mg/L. Concentrations at Piney were still higher however than those reported on un-mined land in the same study in

Ohio. WOCT8 also receives wastewater discharges from a municipal system where potassium alum [$KAl(SO_4)_2 \cdot 12H_2O$] is used in the purification process for the local water supply (Lenntech 2011). Potassium and sulfate ions are dissolved in the purification process and can cycle through the municipal water system and discharged into the receiving stream.

Sulfate and forest cover were significantly and negatively correlated in my study. Research conducted by the USDA Forest Service in the Appalachian Mountains in North Carolina showed that microbial activity in forested soils is capable of incorporating sulfate into soil organic matter through metabolizing sulfate to organic sulfur (Swank et al. 1987). This process can therefore reduce the mobility of the sulfate ion in forested soils, and potentially prevent further transport to streams or groundwater. Transformation of inorganic sulfate to organic sulfate could explain the weak relationship between coal formation and sulfate concentration in WOCT14 which had the largest proportion of coal formation in its sub-catchment yet relatively low sulfate concentrations in its surface water. The remaining sub-catchments in White Oak Creek Watershed did not have significant, or any, coal formation in the sub-catchments, which was reflected in low sulfate concentrations.

4.1.5. Organic Carbon and Nitrogen Concentrations

Dissolved organic carbon (DOC) is a continuum of organic molecules that fit through a 0.45 µm filter (Thurman 1986) and is therefore not necessarily dissolved, but is a range of carbon-based compounds which exhibit a wide range of biodegradability (McDowell et al. 2006) and recalcitrance (Johnson et al. 2011) and are fundamental to

processes in the global carbon cycle (Cole et al. 2007). Dissolved organic nitrogen (DON) typically considered a subset of DOC is a range of carbon molecules that contain an amino-group. Dissolved organic carbon and DON showed similar patterns among the sub-catchments studied. Highest DOC concentrations were found in WOCT7, WOCT3, Lewis and Crosstimber and highest DON concentrations were found in the same sub-catchments plus WOCT8. Both DOC and DON were negatively correlated with barren land and DOC was negatively correlated with deciduous and evergreen forests. On the other hand DOC was positively correlated with low, medium, and high urban development, while DON was positively correlated with pastured land. Sub-catchment WOCT8 supported the findings of Aitkenhead-Peterson et al. (2009) where sub-catchments sampled downstream of a WWTP displayed higher mean concentrations of DOC than those sub-catchments without a WWTP. Sub-catchment WOCT8, sampled downstream of a WWTP had significantly higher mean annual DOC concentrations than eight of the other sub-catchments in the White Oak Creek watershed, but five sub-catchments without a WWTP had higher mean concentrations than WOCT8 suggesting that wastewater effluent alone cannot explain DOC inputs to surface waters. There are two sources of dissolved organic matter (DOM) to surface waters, allochthonous (from the watershed) and autochthonous (within the surface water) with the majority of DOC typically derived from allochthonous sources (Aitkenhead-Peterson et al. 2003). Type of land cover has been implicated in high DOC concentrations and exports (Aitkenhead-Peterson and McDowell 2000) with peatland and wetland typically responsible for higher DOC concentrations and exports (Aitkenhead et al. 1999; Malcolm and Durum

1976) Wetlands in the White Oak Creek subcatchments ranged from 2.1% in WOCT2 to 31.2% in WOCT9 yet the surface water DOC concentrations were not significantly different between the two watersheds suggesting that in the White Oak Creek wetlands do not have much of an impact on surface water DOC concentrations. Mean annual concentrations of DOC which ranged from 6±2 mg/L at WOCT14 to 14.6±.5 mg/L at Lewis were lower than those reported for a rural to urban land use gradient in south-central Texas which ranged from 20.4 to 52.5 mg/L (Aitkenhead-Peterson et al. 2009) but higher than those observed in rangeland and urban sub-catchments of the upper Trinity River basin, TX which ranged from 5.7 to 6.4 mg/L (Aitkenhead-Peterson and Steele 2012). At a land cover scale, DOC concentrations in humid temperate northern mixed forests streams typically range from 2 to 20 mg/L (Clair et al. 1994; Campbell et al. 2000) in tropical forest streams from 1.5 to 4.4 mg/L (Lewis et al. 1999; McDowell and Asbury 1994) and in Scottish rangeland streams from 1.2 to 10.6 mg/L with the major contribution coming from soil carbon deposits stored in peat (Aitkenhead et al. 1999).

Relatively less research has been conducted on streamwater DON relative to that conducted on stream DOC over the last three decades. While DOC and DON are generally highly correlated, particularly in relatively undisturbed watersheds (McDowell 2003) some uncoupling or lack of correlation has been observed over the last decade (McDowell 2003). In the White Oak Creek sub-catchments DOC and DON showed a significant, strong positive correlation ($R = 0.86$ $p < 0.001$) suggesting that the stream chemistry is what should be expected in watersheds not severely impacted by

anthropogenic activities. Another indicator of relatively undisturbed watersheds is the DON:TDN ratio which is a measure of the relative proportion of organic to inorganic nitrogen in surface waters. In the White Oak Creek sub-catchments the DON:TDN ratio ranged from 0.12±11 in WOCT12 which is indicative of high anthropogenic inputs of in-organic nitrogen to 0.71±0.15 in Crosstimber which is indicative of a relatively undisturbed watershed. In a study of 348 streams with varying land use and land management Pellerin et al. (2006) suggested that DON:TDN ratios < 0.35 indicated streams with urban impacts and DON:TDN ratios of > 0.55 indicated forested streams with little anthropogenic impact. In the White Oak Creek sub-catchments mean annual DON concentrations were significantly and positively correlated with pasture ($R = 0.67$; $p = 0.01$) and not urban land cover as DOC was. Those sub-catchments with the highest DON concentrations all have >35 % pastured land within their watershed. Pastured land is largely grazed by cattle in the northeast region of Texas and sub-catchments (WOCT7, WOCT8, WOCT3, Lewis, and Crosstimber) with high proportions of pasture in their watershed and high mean annual concentrations of DON are likely a result of the organic nitrogen found in manure. Additionally, both WOCT7 and WOCT8 sub-catchments contain dairy farms with permitted discharge that may also be a source of organic nitrogen to their surface waters. Agricultural soils with high DON concentrations were observed in a study conducted near the city of Munster, Germany where significant correlation was found between DON in soil leachate and agriculture (Siemans and Kaupenjohann 2002). Mean annual DON concentrations in the White Oak Creek sub-catchments ranged from 0.16±0.10 in WOCT12 to 0.69±0.20 in Crosstimber and these

concentrations are typical of those observed globally for undisturbed watersheds. For example, surface water DON concentrations in mixed northern forests range from 0.12 to 0.37 mg/L (Campbell et al. 2000) and from 0.11 to 0.16 in tropical forest surface waters (Lewis and Saunders 1990; McDowell and Asbury 1994).

4.1.6 Turbidity and Total Suspended Solids

Values for turbidity and total suspended solids (TSS) varied widely between the sub-catchments and generally high TSS values were also reflected in high turbidity values within the same sub-catchment. Differences in soil properties can usually explain any discrepancy, as the size, weight, and refractive properties of the type of suspended sediment can vary which will determine the degree of turbidity. Consistent with previous studies (Brisbois et al. 2008; Chua et al. 2009; Vink et al 2007; Sheeder and Evans 2004), both turbidity and TSS were positively and significantly correlated with pasture land use and negatively correlated with evergreen forest. Vink et al. (2007) examined nutrient and TSS exports from forested and agricultural catchments in southeastern Australia and found TSS concentrations for pastured land significantly higher than those of forested land at 148 mg/L and 29 mg/L, respectively. Similarly, WOCT8 had the highest percentage of pasture (66%), and had the highest mean annual TSS concentrations at 128±105.5 mg/L and WOCT14 with the highest forest land cover (43%) had one of the lowest mean annual TSS concentrations at 61±16.8 mg/L. Cattle manure from dairy farms or other pastures in the sub-catchment may play a critical role in the elevated TSS concentrations. Soupir et al. (2006), observed in their study in Virginia, USA on the effects of P-based manure application on TSS and nutrient

transport on pasture land that TSS concentrations from plots treated with cowpies (preserved cattle manure) were significantly higher than the control due to the breakdown of the cowpies from the rainfall impact. TSS concentrations in the runoff from cowpie plots ranged from 72 to 189 mg/L, producing the highest TSS concentration out of liquid dairy slurry, turkey litter, and the control plot. Additionally, it is not uncommon for cattle grazing on pasture land to have direct access to streams for their water source (Belsky et al.1999). As a result, fecal matter is directly deposited into the stream along with eroded sediment from stream bank disturbance, and increased sediment transport from overland flow in the near stream area where compaction from cattle access has reduced soil infiltration capacity in the riparian zone (Belsky et al. 1999).

4.2 Land Use and Land Management Effects on Surface Water Chemistry

Stream chemistry, a result of biogeochemical cycling in small watersheds was described by Likens and Borman (1974) as geological, meteorological and biological vectors. Their descriptors loosely follow Jenny's (1941) descriptors of soil forming factors which are time, climate, geology, biology and topography. In 2005 Aitkenhead-Peterson et al. suggested these same factors could be used to describe DOC in surface waters and adopting this analogy, Perakis and Hedin (2007) coined the term "State Factors" to describe the components that were most important to describe chemical constituents in surface waters. Therefore comparison of land use and land management practices and their impacts to surface water chemistry can be difficult given differences

in other state factors such as geology, topography and climate, but comparison is valuable for providing a basis for observations among different watersheds in different climatic zones. The benefit of my study which examined 15 sub-catchments underlain by a similar geology and climatic zone meant that the effect of land cover, land use and land management practices could be observed readily without the implications of different geology and climate which might be responsible for differences observed in similar land uses reported in other studies. Overall my study indicated that there are significant differences among the sub-catchments as a result of different land uses and land management practices, and that these differences are generally aligned to similar studies addressing land use and surface water chemistry (e.g. Lenat and Crawford 1993; Goolsby et al. 2001).

Urbanization in watershed studies has gained much attention over the last decade (Williams et al. 2005; Lewis et al. 2007; Sickman et al. 2007; Aitkenhead-Peterson et al. 2009; Petrone 2010; Steele et al. 2010; Aitkenhead-Peterson et al. 2011; Paul & Meyer 2001). In my study, urban land use resulted in significant correlations with salinity (quantified as electrical conductivity), ammonium-N, calcium, magnesium and DOC. Ammonium-N in the Chicago area had mean annual concentrations of 0.2 mg/L (Goolsby et al. 2001), which was slightly lower than observed in my most urbanized sub-catchment. Salinity was associated with increased urbanization in North Carolina when compared to watersheds dominated by forest and agriculture with concentrations of 85 µS/cm in urban watersheds compared to values of 60 and 65 µS/cm in forested and agricultural watersheds (Lenat and Crawford 1993). Electrical conductivity (EC) was

much lower in the North Carolina watersheds compared to my observed EC which ranged from 146±64 to 638±198 µS/cm. Lewis et al. (2007) also reported lower EC values for urban sub-catchments in the Big Brushy Creek watershed in South Carolina with values ranging from 65 to 80 µS/cm and values ranging from 55 to 60 µS/cm in rural sub-catchments. While EC was clearly higher in urban relative to rural sub-catchments, the difference between surface water EC in South Carolina watersheds and White Oak Creek clearly illustrates how other state factors such as the geology underlying a sub-catchment might compromise ones interpretation. .

Dissolved organic carbon concentrations can be highly variable with land use, while my study found that DOC is positively correlated to urban land use, supporting studies by Aitkenhead-Peterson et al. (2009), research by Molinero and Burke (2009) found positive correlations between DOC and pasture land which they attributed to agricultural practices which enriched organic matter in the near stream area.

Increases in forested land cover resulted in decreases in surface water nitrate-N, orthophosphate-P, sulfate, DOC, TSS and turbidity. In contrast to my findings, other studies reported a positive correlation between DOC and forest land cover in a Michigan watershed (Molinero and Burke 2009) and in a forested catchment in south eastern Australia (Vink et al. 2007). Both studies accredited the addition of leaf litter to nearby streams for the higher DOC concentrations observed. Decreases observed in nitrate-N, soluble phosphate-P, and sulfate in surfaces waters with a high proportion of forest cover may be a result of attenuation in forest soils as indicated by Ranalli and Macalady (2010) and Swank et al. (1987) where nitrate and sulfate concentrations were significantly

reduced in riparian and forested areas through plant/vegetation uptake and immobilization or transformation by microorganisms. Both sulfate and nitrate can serve as electron acceptors under anaerobic conditions found in riparian soils. My observation of declining orthophosphate-P with increased forest cover supports other land use catchment studies which report negative correlations between orthophosphate and forest cover and positive correlations between orthophosphate and agricultural land use (Nimiroski et al. 2008; Sussman 1983; Chen and Driscoll 2009).

The affect of agricultural land use in a watershed will depend upon the type of agriculture (crop or husbandry) and best management practices in operation to reduce runoff to surface waters. Land used for pasture showed a significant positive correlation with surface water orthophosphate-P in my study supporting findings of other researchers (Vink et al. 2007; Ballantine et al. 2009; Knowlton et al. 2006). Pastures also showed positive correlations with DON, TSS and turbidity and a negative correlation with the DON:TDN ratio. DON had a positive correlation to pasture and grazed cattle land relative to other land uses in a Georgia Piedmont watershed with DON concentration for the pastured land ranging from 0.22 to 0.84 mg/L (Molinero and Burke 2009). TSS and turbidity concentrations were also linked to pastures in agricultural land use studies (Brisbois et al. 2008; Vink et al. 2007).

Overall land management practices in the White Oak Creek watershed reflect what has been observed in other studies researching urban, agricultural, and forested land uses. Results from my study are valuable in that they provide a comparison for other regions with similar land uses. Nutrient concentrations from my study can be used

to further determine areas of excessive nutrient concentrations relative to those observed in other regions and seek better alternatives for land best management practices.

4.3 Exports of Nutrients in a Rangeland Watershed

There is relatively little up to date information on loads and exports of DOC, DON, anions and cations from sub-tropical rangelands. Most interest in DOC and DON exports has centered around forested and peatland watersheds (Clair et al. 1994; Kortelainen et al. 1997; Aitkenhead-Peterson et al. 2005; Aitkenhead-Peterson et al. 2007) because of the perceived loss of sequestered carbon in watershed soils and more recently because of observations in long-term data of increasing DOC concentrations and exports over the last two decades attributed to land use change, climate change, recovery from acid deposition (Evans et al. 2002; Freeman et al. 2001; Tranvik and Jansson 2002; Worrall et al. 2003; Hongve et al. 2004; Tetzlaff et al. 2007; Garnett et al. 2000; Clark et al. 2005; Sucker and Krause 2011). Loads and exports of chloride and sodium have become important recently in northern watersheds because of the deicing salt issue (Kaushal et al. 2005; Daley et al. 2009). To counter this trend, Aitkenhead-Peterson and Steele (2012) have reported on sub-tropical exports of DOC, DON and DIN from urban and rural watersheds and examined sodium and chloride loadings in sub-tropical watersheds not impacted with deicing salts (Steele and Aitkenhead-Peterson 2011). Cation exports, with the exception of sodium and exports of anions with the exception of chloride and sulfate are rarely reported.

There are several methods to calculate daily loads and annual exports of chemical constituents. In my study I used two typically used methods, the first was linear interpolation of concentrations between sampling dates followed by multiplying daily concentration (mg/L) by average daily export reported for the gauge (L/sec) and multiplying by seconds in a day results in a daily load of chemical constituent, which when summed and divided by watershed area results in annual export per unit area. The second method relies on a relatively strong and significant relationship with discharge and is described in detail in Aitkenhead-Peterson et al. (2005, 2007). In my study I used both methods and report best estimates of exports. It is important to examine loading and exports because White Oak Creek joins the Sulphur River near Texarkana, TX and then flows into Wright Patman Lake impoundment as Texarkana's drinking water supply. Water from Wright Patman Lake is released into the Red River in Louisiana and finally flows into the Mississippi River where it is deposited into the Gulf of Mexico. Goolsby et al. (2001) and Alexander et al. (2004) have examined the increases of nutrient loads to the Gulf of Mexico that have led to conditions of hypoxia spanning an area of 6,765 mi^2 along the gulf (USEPA 2011). Exports of chemical constituents from White Oak Creek were compared to exports reported in the literature for forested and pasture watersheds. Studies showed a range of export values for nitrogen in forested watersheds. Ammonium-N exports ranged from 0.61 to 39.0 $kg/km^2/yr$ in forested watersheds (Chen and Driscoll 2009; Lewis et al. 1999; Vink et al. 2007) which suggests that ammonium-N exports in White Oak Creek at 4.7 $kg/km^2/yr$ are relatively low compared to other studies. Nitrate-N in forested watersheds ranged from 15 to 243 $kg/km^2/yr$ (Chen and

Driscoll 2009; Lewis et al. 1999; Vink et al. 2007) and compared to my estimated export of nitrate-N of 54.4 kg/km^2/yr suggests that loss of nitrate-N from White Oak Creek is not a major issue. Typically older forests do not utilize soil nitrate as well as younger forests and it is typical to observe higher nitrate export from older forests relative to younger forests. Land management practices such as strip and clear-cutting for timber harvest also have an effect on increasing nitrate export because of soil aeration and increased precipitation reaching watershed soils resulting in higher runoff. Watersheds with pasture as the dominant land use have fewer reports of inorganic-N exports. Vink et al. (2007) reported ammonium-N exports of 1.6 kg/km^2/yr and nitrate-N exports of 3.4 kg/km^2/y in a pastured watershed in south-eastern Australia which were much lower than my exports. My watershed had almost 55% of its land use under pasture and this comparison suggests that management practices should be put into place to mitigate enhanced ammonium-N and nitrate-N export from White Oak Creek watershed. Where nitrate-N was the dominant N species exported from White Oak Creek, DON was the next exporting 17 kg/km^2/yr. The literature on DON export from agricultural watersheds is relatively sparse. Van Kessel et al. (2009) suggested that DON exports from agricultural watersheds are largely ignored despite the effect they have on eutrophication and acidification of surface waters. Van Kessel et al. (2009) reported exports ranging from 3.5 to 4.3 kg/km^2/yr from watersheds dominated by pasture, fertilized with inorganic-N in Northern Ireland. Exports of DON in White Oak Creek were almost 5 times higher than those observed in Northern Ireland and suggests that perhaps land management practices such as restricted access to cattle to surface water and rotational

grazing may help reduce DON exports at White Oak Creek. Another factor of course is climatic differences, higher temperatures and lower precipitation in sub-tropical ecosystems result likely result in higher microbial activity which releases more DON in the dissolved form. A second theory, though not tested, is that increased pH in watershed soils may solubilize DON more readily than watersheds with a lower pH expected in Northern Ireland. Export of phosphate-P from watersheds dominated by pasture is relatively low at 0.95 kg/km^2/yr in Australia (Vink et al. 2007). Export from White Oak Creek was over three times higher at 3.2 kg/km^2/yr. The combination of organic nitrogen from manure and annual fertilizer additions to pastures in my study watershed may explain the higher exports than those observed in the study in Australia where pastures were reported as unfertilized.

Similar to other exports, little has been reported for dissolved organic carbon from pastures (Vink et al. 2007). The export at White Oak Creek was 371 kg/km^2/yr slightly lower than the 577 kg/km^2/yr reported by Vink et al. (2007). Dissolved organic carbon concentrations and exports have been shown to be driven by allochthonous exports such as soil and litter (Aitkenhead-Peterson et al. 2003). .

Many of the study sites examined for cation export are reported from watersheds in the north where deicing salts are applied and are dominated by forest land use. Chen and Driscoll (2009) reported estimated cation exports assuming 100% agricultural land cover of 48,000 calcium kg/km^2/yr, 12,500 magnesium kg/km^2/yr and 2, 400 potassium values that were about two orders of magnitude higher than I found at White Oak Creek. Bear in mind that their estimates are just estimates, and I feel do not describe realistic

cation exports from watersheds underlain by shales and sandstones. Similar to cation exports from sub-tropical rangeland, no reasonable estimates have been published for exports of chloride and sulfate. Chen and Driscoll (2009) estimated that watersheds underlain by shale and sandstone and having 100% agriculture would export 25,000 $kg/km^2/yr$ sulfate and did not estimate export of chloride. Sulfate export estimates by Chen and Driscoll (2009) were an order of magnitude greater than the exports observed at White Oak Creek (1916 $kg/km^2/yr$). Jeje (2006) reported that TSS exports from watersheds with pasture as the dominant land use was 51,450 $kg/km^2/yr$ again an order of magnitude higher than observed at White Oak Creek.

5. CONCLUSION

5.1 Limitations of Study

There were several limitations to this study that prevented a more comprehensive assessment of stream chemistry and land use within the White Oak Creek Watershed. Low flow conditions during summer months prevented sampling at certain sites, limiting the data available. Transport of biological oxygen demand samples from the site to the laboratory may have caused some disturbance in dissolved oxygen saturation, preventing observation of more significant findings for this parameter.

5.2 Conclusion

This study has highlighted several important water quality management issues for rural watersheds. Additionally, this study advanced the knowledge of mean annual concentrations and exports of nutrients in a south-central, sub-tropical rangeland ecosystem. Overall, the data from this study suggests that a rural, dominantly pastured watershed does not lead to excessive nutrient concentrations in adjacent stream waters. Specifically, when compared to other research on land use activities and land management impacts to surface water chemistry, I found that:

- Nitrate-N concentrations in my forested and urban catchments were comparable to those found in other studies, while agricultural, pastured land use in my watershed were lower than those reported by other studies on agricultural catchments, and much lower than those reported with dominant row crop agriculture.

- Concentrations of orthophosphate-P in my watershed were comparable to other watershed studies with effluent inputs and fertilized pastured land.
- Cation concentrations in my watershed were found to be typical of what you would expect in this region of Texas, with natural sources such as bedrock geology providing the dominant inputs.
- Chloride and fluoride concentrations were observed to be lower than what has been observed in many other watersheds. While sulfate concentrations were observed to be higher than un-mined watersheds, but lower than those concentrations reported for abandoned and previously mined land.
- Dissolved organic carbon concentrations were lower than those reported in areas of south central Texas, but slightly higher than what has been reported for other areas in northeast Texas. Dissolved organic nitrogen concentrations were largely comparable to what has been reported for undisturbed watersheds globally.
- Total suspended solids and turbidity concentrations were observed to be comparable to other studies, and also showed consistency with other studies with higher concentrations reported in pastured land, and lower concentrations in forested land.

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APPENDICES

Appendix 1. Raw data for sub-catchments pH, electrical conductivity (µS/cm) and nutrients (mg/L)

Date	NAWA ID	Sample ID	Creek #	pH	EC	NH_4-N	NO_3-N	PO_4-P	$CaCO_3$
					µS/cm			mg/L	
4/5/2010	3372	Crosstimber	1	7.31	580	0.07	0.10	0.02	105
5/17/2010	3423	Crosstimber	1	7.56	170	0.10	0.49	0.05	56
6/2/2010	3502	Crosstimber	1	7.10	160	0.13	0.29	0.06	92
6/24/2010	3562	Crosstimber	1	7.60	102	0.09	0.39	0.05	66
7/23/2010	3593	Crosstimber	1	7.10	150	0.13	0.14	0.03	54
9/26/2010	3661	Crosstimber	1	7.50	130	0.09	0.20	0.08	35
10/30/2010		Crosstimber	1	7.00	190	0.05	0.06	0.02	77
1/19/2011	4249	Crosstimber	1	7.60	170	0.08	0.05	0.19	55
2/19/2011	4373	Crosstimber	1	6.40	130	0.08	0.06	0.17	72
3/25/2011	4456	Crosstimber	1	7.30	210	0.10	0.09	0.08	103
4/5/2010	3374	Lewis	2	7.11	450	0.17	0.12	0.03	39
5/17/2010	3424	Lewis	2	7.20	185	0.19	0.34	0.13	35
6/2/2010	3503	Lewis	2	6.90	409	0.28	0.29	0.02	71
6/24/2010	3558	Lewis	2	7.10	310	0.18	0.16	0.02	67
7/23/2010	3595	Lewis	2	7.20	300	0.27	0.13	0.03	56
1/19/2011	4254	Lewis	2	6.90	250	0.07	0.05	0.06	45
3/25/2011	4460	Lewis	2	6.60	230	0.11	0.10	0.06	66
4/5/2010	3373	Piney	3	7.17	740	0.06	0.05	0.03	43
5/17/2010	3422	Piney	3	7.34	587	0.16	0.11	0.04	41
6/2/2010	3504	Piney	3	7.30	160	0.21	0.15	0.01	55
6/24/2010	3552	Piney	3	7.60	297	0.08	0.10	0.02	45
7/23/2010	3596	Piney	3	7.10	300	0.09	0.34	0.03	50
10/9/2010	3689	Piney	3	7.30	540	0.08	0.09	0.03	125
10/30/2010	3719	Piney	3	7.30	450	0.04	0.06	0.18	34
12/11/2010	4189	Piney	3	7.20	410	0.06	0.07	0.02	51

1/19/2011	4255	Piney	3	7.60	350	0.09	0.19	0.03	35
2/19/2011	4366	Piney	3	7.00	660	0.08	0.10	0.04	56
3/25/2011	4465	Piney	3	6.70	710	0.08	0.08	0.02	75
6/2/2010	3505	Ripley	4	7.10		0.16	0.26	0.02	56
6/24/2010	3550	Ripley	4	6.90	620	0.13	0.24	0.02	44
7/23/2010	3594	Ripley	4	7.30	660	0.13	0.14	0.02	60
9/26/2010	3660	Ripley	4	7.40	490	0.12	0.12	0.03	47
10/9/2010	3680	Ripley	4	7.20	470	0.07	0.12	0.04	119
10/30/2010	3717	Ripley	4	7.40	250	0.06	0.18	0.07	54
12/11/2010	4176	Ripley	4	7.50	360	0.08	0.06	0.04	255
1/19/2011	4260	Ripley	4	7.40	290	0.07	0.18	0.09	48
3/25/2011	4461	Ripley	4	7.50	580	0.09	0.09	0.03	82
4/5/2010	3361	WOCT1	8	7.10	430	0.17	0.18	0.07	62
5/17/2010	3408	WOCT1	8	7.07	356	0.15	0.49	0.06	57
6/24/2010	3554	WOCT1	8	7.10	175	0.10	0.21	0.06	45
6/2/2010	3491	WOCT1	8	7.50	244	0.07	0.36	0.07	29
7/23/2010	3601	WOCT1	8	6.80	150	0.15	0.23	0.05	40
9/26/2010	3662	WOCT1	8	7.20	160	0.12	0.12	0.05	45
10/9/2010	3685	WOCT1	8	7.20	150	0.14	0.17	0.04	65
10/30/2010	3714	WOCT1	8	6.70	150	0.11	0.11	0.17	33
12/11/2010	4175	WOCT1	8	7.10	180	0.04	0.05	0.04	489
1/19/2011	4246	WOCT1	8	8.20	170	0.07	0.14	0.05	81
2/19/2010	4370	WOCT1	8	7.30	200	0.06	0.06	0.05	90
3/25/2010	4458	WOCT1	8	6.90	260	0.09	0.09	0.05	106
5/17/2010	3415	WOCT10	9	7.20		0.26	0.21	0.03	57
6/2/2010	3498	WOCT10	9	6.80		0.12	0.15	0.01	45
6/24/2010	3547	WOCT10	9	6.90	228	0.19	0.21	0.01	28
7/23/2010	3591	WOCT10	9	6.90	190	0.11	0.22	0.01	42
9/26/2010	3667	WOCT10	9	7.40	140	0.10	0.35	0.37	50
10/30/2010	3710	WOCT10	9	6.50	90	0.04	0.06	0.08	27
1/19/2011	4253	WOCT10	9	6.90	80	0.07	0.12	0.02	9
5/17/2010	3416	WOCT12	10	7.47	248	0.12	0.85	0.07	36
6/2/2010	3499	WOCT12	10	7.30	227	0.13	0.65	0.04	38

6/24/2010	3564	WOCT12	10	6.90	283	0.11	0.59	0.05	49
7/23/2010	3603	WOCT12	10	6.90	210	0.08	0.49	0.03	31
9/26/2010	3670	WOCT12	10	7.00	160	0.08	0.17	0.10	20
10/9/2010	3681	WOCT12	10	7.00	170	0.13	0.26	0.04	40
10/30/2010	3716	WOCT12	10	6.90	240	0.05	0.24	0.07	54
12/11/2010	4178	WOCT12	10	6.80	200	0.07	0.35	0.02	190
1/19/2011	4259	WOCT12	10	7.10	330	0.08	0.46	0.02	16
2/19/2010	4368	WOCT12	10	6.70	330	0.07	0.24	0.02	26
3/25/2010	4464	WOCT12	10	6.80	360	0.16	0.12	0.03	40
4/5/2010	3364	WOCT13	11	7.21	520	0.19	0.09	0.03	45
5/17/2010	3417	WOCT13	11	6.82	1124	0.17	0.36	0.02	37
6/2/2010	3500	WOCT13	11	7.20	828	0.18	0.21	0.03	60
6/24/2010	3548	WOCT13	11	6.90	470	0.16	0.16	0.03	8
7/23/2010	3589	WOCT13	11	7.10	590	0.22	0.13	0.03	63
9/26/2010	3669	WOCT13	11	7.20	720	0.18	0.10	0.09	79
10/9/2010	3682	WOCT13	11	7.10	750	0.18	0.10	0.08	108
10/30/2010	3711	WOCT13	11	7.00	520	0.07	0.06	0.05	48
12/11/2010	4183	WOCT13	11	7.20	430	0.04	0.05	0.04	107
1/19/2011	4258	WOCT13	11	7.10	450	0.07	0.12	0.02	28
2/19/2010	4369	WOCT13	11	6.60	590	0.05	0.06	0.01	35
3/25/2010	4466	WOCT13	11	6.70	660	0.07	0.07	0.03	67
5/17/2010	3418	WOCT14	12	7.14		0.10	0.32	0.02	68
6/2/2010	3501	WOCT14	12	7.30	850	0.09	0.32	0.02	72
6/24/2010	3559	WOCT14	12	7.20	372	0.09	0.39	0.04	77
7/23/2010	3600	WOCT14	12	7.20	370	0.10	0.21	0.03	66
9/26/2010	3666	WOCT14	12	7.30	340	0.07	0.11	0.04	54
10/9/2010	3691	WOCT14	12	7.20	210	0.07	0.16	0.04	64
10/30/2010	3704	WOCT14	12	7.00	220	0.06	0.14	0.05	44
12/11/2010	4180	WOCT14	12	7.20	330	0.05	0.35	0.05	66
1/19/2011	4257	WOCT14	12	7.50	310	0.14	0.32	0.06	34
2/19/2010	4376	WOCT14	12	7.10	480	0.06	0.19	0.02	65
3/25/2010	4453	WOCT14	12	7.10	510	0.11	0.11	0.03	92
4/5/2010	3362	WOCT3	13	7.58	450	0.19	0.25	0.02	82

5/17/2010	3410	WOCT3	13	7.65		0.18	0.32	0.05	89
6/2/2010	3493	WOCT3	13	7.00	320	0.12	0.18	0.04	85
6/24/2010	3557	WOCT3	13	7.50	450	0.07	0.08	0.02	109
7/23/2010	3597	WOCT3	13	7.10	310	0.13	0.07	0.05	100
9/26/2010	3664	WOCT3	13	7.40	240	0.18	0.17	0.16	70
10/9/2010	3687	WOCT3	13	7.20	290	0.09	0.09	0.03	133
10/30/2010	3715	WOCT3	13	6.80	120	0.17	1.32	0.09	35
12/11/2010	4187	WOCT3	13	7.10	200	0.06	0.05	0.08	62
1/19/2011	4248	WOCT3	13	7.50	140	0.08	0.17	0.07	115
2/19/2010	4379	WOCT3	13	6.60	140	0.08	0.17	0.09	72
4/5/2010	3363	WOCT6	14	7.21	670	0.24	0.06	0.01	70
5/17/2010	3411	WOCT6	14	7.27	417	0.22	0.11	0.03	83
6/2/2010	3494	WOCT6	14	7.10	410	0.16	0.49	0.01	93
6/24/2010	3551	WOCT6	14	7.40	569	0.07	0.06	0.01	59
7/23/2010	3598	WOCT6	14	7.20	350	0.15	0.04	0.01	98
9/26/2010	3664/3659	WOCT6	14	7.50	300	0.12	0.12	0.02	69
10/9/2010	3688	WOCT6	14	7.50	320	0.47	0.09	0.04	131
10/30/2010	3708	WOCT6	14	7.20	290	0.12	0.06	0.03	87
12/11/2010	4179	WOCT6	14	7.20	350	0.07	0.23	0.06	68
1/19/2011	4250	WOCT6	14	7.60	170	0.08	0.08	0.05	50
2/19/2010	4374	WOCT6	14	6.50	120	0.08	0.06	0.06	62
3/25/2010	4452	WOCT6	14	6.70	220	0.13	0.13	0.05	77
5/17/2010	3412	WOCT7	15	7.20		0.17	1.06	2.06	38
6/2/2010	3495	WOCT7	15	7.30	540	0.10	0.49	0.14	71
6/24/2010	3556	WOCT7	15	7.50	423	0.12	0.27	0.20	98
7/23/2010	3604	WOCT7	15	7.40	500	0.10	0.19	0.22	106
12/11/2010	4177	WOCT7	15	7.20	380	0.05	0.06	0.11	229
2/19/2010	4373	WOCT7	15	6.80	460	0.17	1.26	0.26	69
3/25/2010	4459	WOCT7	15	7.40	580	0.26	0.22	0.07	122
5/17/2010	3413	WOCT8	16	7.03		0.17	0.73	0.09	63
6/2/2010	3496	WOCT8	16	7.10	700	0.12	0.28	0.09	127
6/24/2010	3549	WOCT8	16	7.10	747	0.12	0.22	0.04	60
7/23/2010	3590	WOCT8	16	7.20	760	0.15	0.16	0.05	77

9/26/2010	3665	WOCT8	16	7.80	830	0.36	0.12	0.09	124
10/9/2010	3684	WOCT8	16	7.40	810	0.17	0.31	0.09	149
10/30/2010	3713	WOCT8	16	7.10	320	0.08	0.17	0.07	46
12/11/2010	4184	WOCT8	16	7.20	490	0.06	0.05	0.07	67
1/19/2011	4251	WOCT8	16	7.50	270	0.31	1.03	0.17	34
2/19/2010	4372	WOCT8	16	7.40	470	0.12	0.83	0.12	82
3/25/2010	4463	WOCT8	16	7.30	660	0.10	0.08	0.09	106
5/17/2010	3414	WOCT9	17	7.35		0.17	0.23	0.08	74
6/2/2010	3497	WOCT9	17	7.00	210	0.08	0.11	0.04	61
6/24/2010	3553	WOCT9	17	7.80	469	0.07	0.36	0.05	59
7/23/2010	3599	WOCT9	17	6.90	350	0.10	0.07	0.03	74
9/26/2010	3657	WOCT9	17	8.00	610	0.11	1.03	0.27	107
10/30/2010	3712	WOCT9	17	7.30	170	0.07	0.58	0.22	38
12/11/2010	4188	WOCT9	17	7.50	610	0.06	1.81	0.32	97
1/19/2011	4252	WOCT9	17	7.70	290	0.28	1.13	0.30	73
2/19/2010	4365	WOCT9	17	7.30	340	0.10	0.89	0.20	87
3/25/2010	4462	WOCT9	17	6.80	390	0.12	0.14	0.10	98
5/17/2010	3409	WOCT2	18	6.98		1.01	2.24	0.31	77
6/2/2010	3492	WOCT2	18	7.10	110	0.09	0.32	0.06	26
6/24/2010	3563	WOCT2	18	7.40		0.06	0.07	0.21	123
9/26/2010	3658	WOCT2	18	7.40	160	0.51	1.51	0.32	30
10/30/2010	3705	WOCT2	18	7.10	240	0.09	0.45	0.19	72
12/11/2010	4186	WOCT2	18	7.20	310	0.12	0.26	0.13	50
1/19/2011	4247	WOCT2	18	7.70	220	0.55	1.58	0.44	67
2/19/2010	4367	WOCT2	18	7.20	630	0.11	2.21	0.12	119
3/25/2010	4455	WOCT2	18	6.90	720	0.27	0.12	0.14	152

Appendix 2 Raw data for subcatchment cations and anions.

Date	NAWA ID	Sample ID	Creek #	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
							mg/L				
4/5/2010	3372	Crosstimber	1	20.02	6.45	14.98	24.10	0.19	27.18	1.67	54.30
5/17/2010	3423	Crosstimber	1	11.71	4.44	7.30	15.56	0.17	13.11	1.52	17.68
6/2/2010	3502	Crosstimber	1	35.95	4.11	4.44	10.47	0.25	16.95	0.78	15.24
6/24/2010	3562	Crosstimber	1	22.39	4.45	4.91	11.96	0.27	14.18	0.68	13.23
7/23/2010	3593	Crosstimber	1	11.11	4.60	5.49	13.07	0.23	9.10	4.14	7.81
9/26/2010	3661	Crosstimber	1	23.41	1.74	2.30	7.94	0.12	10.20	0.21	14.29
10/30/2010		Crosstimber	1	18.52	7.01	6.64	15.61	0.21	9.16	5.55	9.01
1/19/2011	4249	Crosstimber	1	9.15	7.18	6.06	15.64	0.00	6.49	0.50	16.32
2/19/2011	4373	Crosstimber	1	21.32	4.74	4.39	11.73	0.27	11.32	1.93	12.66
3/25/2011	4456	Crosstimber	1	12.38	6.46	8.15	22.61	0.25	12.65	0.12	13.63
4/5/2010	3374	Lewis	2	33.33	5.74	6.74	13.75	0.09	45.02	0.32	50.37
5/17/2010	3424	Lewis	2	19.57	4.39	4.31	11.55	0.05	26.30	1.28	23.81
6/2/2010	3503	Lewis	2	32.17	4.36	8.60	21.79	0.17	39.24	0.84	46.64
6/24/2010	3558	Lewis	2	37.07	4.17	6.97	19.32	0.18	33.88	0.47	38.28
7/23/2010	3595	Lewis	2	28.93	5.39	7.85	21.14	0.10	32.32	4.51	34.24
1/19/2011	4254	Lewis	2	22.17	6.80	4.83	12.77	0.02	20.10	3.58	18.40
3/25/2011	4460	Lewis	2	26.60	5.16	6.21	18.63	0.20	37.58	0.14	22.02
4/5/2010	3373	Piney	3	44.09	6.63	14.52	22.42	0.17	47.48	1.05	128.13
5/17/2010	3422	Piney	3	64.17	5.33	15.15	28.22	0.25	61.26	1.94	152.43
6/2/2010	3504	Piney	3	60.20	5.47	16.00	27.37	0.27	61.54	0.42	141.98
6/24/2010	3552	Piney	3	26.70	3.04	5.47	14.31	0.20	20.20	0.13	36.47
7/23/2010	3596	Piney	3	22.60	5.08	7.50	18.49	0.20	22.64	4.30	44.78
10/9/2010	3689	Piney	3	53.04	4.53	7.48	11.56	0.24	38.31		73.33
10/30/2010	3719	Piney	3	44.84	5.65	9.88	21.55	0.14	28.25	17.83	
12/11/2010	4189	Piney	3	42.59	7.10	10.40	19.96	0.09	31.03	3.76	98.19
1/19/2011	4255	Piney	3	24.25	7.02	10.08	24.39	0.04	29.49	2.38	81.09
2/19/2011	4366	Piney	3	50.76	3.81	13.39	27.81	0.15	40.46	2.83	125.93
3/25/2011	4465	Piney	3	62.52	5.86	19.65	43.21	0.24	61.47	3.93	161.65

6/2/2010	3505	Ripley	4	57.46	6.38	14.04	22.07	0.24	61.36	1.11	126.18
6/24/2010	3550	Ripley	4	50.54	6.17	12.44	25.25	0.17	50.09	0.55	112.16
7/23/2010	3594	Ripley	4	62.68	7.05	13.52	25.86	0.08	61.50	4.23	108.75
9/26/2010	3660	Ripley	4	29.91	2.74	4.25	11.81	0.13	18.81	0.13	56.82
10/9/2010	3680	Ripley	4	54.72	3.97	6.73	14.23	0.11	36.87	0.09	80.14
10/30/2010	3717	Ripley	4	43.01	7.16	6.26	14.27	0.15	24.53	24.50	48.77
12/11/2010	4176	Ripley	4	40.29	7.23	8.39	17.58	0.06	41.24	3.32	55.10
1/19/2011	4260	Ripley	4	28.58	7.22	6.33	14.51	0.14	26.51	3.66	41.84
3/25/2011	4461	Ripley	4	66.91	7.42	15.27	34.20	0.22	55.59	4.59	121.74
4/5/2010	3361	WOCT1	8	23.98	8.54	8.49	17.97	0.30	22.53	0.39	40.49
5/17/2010	3408	WOCT1	8	20.61	4.96	6.69	17.16	0.10	23.98	1.73	34.34
6/24/2010	3554	WOCT1	8	25.35	3.55	4.21	10.37	0.19	16.33	0.49	26.34
6/2/2010	3491	WOCT1	8	8.15	4.47	2.79	8.07	0.09	9.04	1.25	13.64
7/23/2010	3601	WOCT1	8	11.91	4.64	4.35	11.63	0.16	13.59	3.55	14.07
9/26/2010	3662	WOCT1	8	20.72	2.50	2.07	8.10	0.19	9.01	0.11	13.87
10/9/2010	3685	WOCT1	8	29.03	4.74	5.12	13.46	0.19	19.15	0.34	60.07
10/30/2010	3714	WOCT1	8	28.61	6.02	3.74	11.24	0.18	14.11	3.31	19.95
12/11/2010	4175	WOCT1	8	19.87	6.50	5.77	16.36	0.08	12.76	4.10	24.18
1/19/2011	4246	WOCT1	8	13.25	4.54	4.24	14.11	0.14	9.37	3.09	14.52
2/19/2010	4370	WOCT1	8	31.17	4.42	4.04	14.24	0.18	19.91	3.52	19.42
3/25/2010	4458	WOCT1	8	22.69	5.95	6.91	24.69	0.19	20.19	0.07	23.25
5/17/2010	3415	WOCT10	9	34.71	5.02	5.96	11.49	0.24	18.95	0.43	47.40
6/2/2010	3498	WOCT10	9	16.77	6.17	7.99	16.13	0.19	9.00	0.25	50.92
6/24/2010	3547	WOCT10	9	16.23	5.68	7.24	15.09	0.16	7.98	0.49	58.66
7/23/2010	3591	WOCT10	9	18.81	5.45	7.95	15.56	0.21	16.07	3.86	45.11
9/26/2010	3667	WOCT10	9	20.31	1.70	1.48	9.21	0.11	8.94	0.18	9.44
10/30/2010	3710	WOCT10	9	33.92	3.77	3.08	7.55	0.15	13.44	17.43	17.19
1/19/2011	4253	WOCT10	9	9.63	3.79	3.20	6.72	0.03	8.33	1.37	17.11
5/17/2010	3416	WOCT12	10	32.66	3.91	7.89	14.31	0.12	36.07	3.04	59.31
6/2/2010	3499	WOCT12	10	25.20	3.84	6.28	12.02	0.17	26.50	1.99	36.45
6/24/2010	3564	WOCT12	10	30.01	4.09	5.68	13.93	0.12	24.79	1.79	38.77
7/23/2010	3603	WOCT12	10	24.50	5.78	5.84	14.74	0.18	25.22	7.07	39.23
9/26/2010	3670	WOCT12	10	33.99	1.47	1.73	5.28	0.07	15.44	0.26	20.08

10/9/2010	3681	WOCT12	10	27.62	3.13	2.91	6.52	0.03	21.74	0.55	30.89
10/30/2010	3716	WOCT12	10	38.84	6.03	5.29	12.23	0.06	27.45	5.25	35.13
12/11/2010	4178	WOCT12	10	20.90	5.65	5.71	10.84	0.03	26.15	3.06	28.47
1/19/2011	4259	WOCT12	10	27.98	5.60	8.63	17.39	0.03	32.51	2.67	69.22
2/19/2010	4368	WOCT12	10	29.31	3.60	8.34	16.14		32.80	2.48	54.84
3/25/2010	4464	WOCT12	10	29.13	3.10	7.42	16.73	0.07	21.56	0.15	35.78
4/5/2010	3364	WOCT13	11	41.00	5.85	7.96	15.74	0.12	66.42	0.09	50.49
5/17/2010	3417	WOCT13	11	52.10	4.81	14.21	23.84	0.16	54.25	1.23	121.09
6/2/2010	3500	WOCT13	11	43.87	5.48	12.33	21.45	0.25	46.45	0.49	89.00
6/24/2010	3548	WOCT13	11	32.66	3.61	7.60	16.68	0.19	28.16	0.27	63.11
7/23/2010	3589	WOCT13	11	39.54	4.21	8.87	20.42	0.18	37.31	4.02	60.66
9/26/2010	3669	WOCT13	11	47.28	2.18	5.14	12.16		28.42	0.06	76.23
10/9/2010	3682	WOCT13	11	76.46	6.43	13.77	17.83	0.11	66.41	0.25	253.66
10/30/2010	3711	WOCT13	11	63.95	6.16	11.31	21.28	0.13	37.34	6.15	0.00
12/11/2010	4183	WOCT13	11	37.10	7.27	12.61	22.03	0.13	28.90	3.17	107.24
1/19/2011	4258	WOCT13	11	33.21	7.37	11.83	23.48	0.23	53.30	2.06	72.78
2/19/2010	4369	WOCT13	11	50.39	5.29	16.85	31.97	0.14	68.11	0.74	104.53
3/25/2010	4466	WOCT13	11	53.08	5.64	17.68	33.40	0.17	69.13	3.87	89.39
5/17/2010	3418	WOCT14	12	49.30	3.86	10.34	20.00	0.35	73.70	3.47	47.97
6/2/2010	3501	WOCT14	12	43.07	3.77	9.77	18.21	0.19	62.03	0.90	43.61
6/24/2010	3559	WOCT14	12	46.41	5.06	6.97	16.50	0.14	57.39	1.19	28.92
7/23/2010	3600	WOCT14	12	32.61	4.44	7.92	17.34	0.13	46.03	4.48	22.85
9/26/2010	3666	WOCT14	12	33.45	1.51	2.52	8.76	0.27	20.88	0.07	24.83
10/9/2010	3691	WOCT14	12	27.54	1.78	2.69	7.20	0.08	19.60	0.21	23.09
10/30/2010	3704	WOCT14	12	22.12	5.21	4.89	11.09	0.15	21.60	2.61	16.96
12/11/2010	4180	WOCT14	12	42.71	5.10	7.78	17.99	0.09	47.16	4.08	35.96
1/19/2011	4257	WOCT14	12	27.60	5.37	7.16	12.82	0.11	34.94	2.87	32.05
2/19/2010	4376	WOCT14	12	43.99	3.05	10.65	19.09	0.07	66.37	2.99	39.44
3/25/2010	4453	WOCT14	12	57.94	3.66	13.23	25.68	0.07	79.13	0.44	49.77
4/5/2010	3362	WOCT3	13	21.50	5.76	10.52	20.49	0.31	22.71	0.53	44.04
5/17/2010	3410	WOCT3	13	26.78	5.57	11.70	24.45	0.19	29.57	0.83	40.98
6/2/2010	3493	WOCT3	13	17.01	5.94	8.32	21.22	0.24	14.67	0.48	28.93
6/24/2010	3557	WOCT3	13	36.11	5.54	10.91	27.79	0.24	27.97	0.19	38.23

7/23/2010	3597	WOCT3	13	17.11	5.98	8.84	22.63	0.35	13.89	5.37	19.89
9/26/2010	3664	WOCT3	13	23.13	3.16	2.69	13.28	0.35	10.92	0.94	19.41
10/9/2010	3687	WOCT3	13	37.36	4.13	5.45	16.84	0.21	20.84	2.32	39.23
10/30/2010	3715	WOCT3	13	31.89	5.49	3.07	8.30	0.13	14.14	29.66	11.14
12/11/2010	4187	WOCT3	13	16.52	7.97	7.55	15.83	0.07	13.94	2.58	17.61
1/19/2011	4248	WOCT3	13	11.70	6.33	4.26	11.16	0.11	10.60	2.57	18.54
2/19/2010	4379	WOCT3	13	25.38	4.09	4.98	15.97	0.27	16.02	3.70	27.37
4/5/2010	3363	WOCT6	14	38.80	6.49	11.65	21.24	0.26	70.21	0.08	42.71
5/17/2010	3411	WOCT6	14	40.31	4.39	10.49	22.96	0.20	75.41	0.29	24.36
6/2/2010	3494	WOCT6	14	29.52	5.73	9.80	24.37	0.30	52.63	0.11	13.73
6/24/2010	3551	WOCT6	14	33.17	4.10	7.88	20.59	0.25	56.57	3.84	10.06
7/23/2010	3598	WOCT6	14	28.50	4.71	8.28	21.37	0.38	35.86	5.89	8.93
9/26/2010	3664/3659	WOCT6	14	33.42	2.38	2.53	8.82	0.36	19.27	0.44	9.86
10/9/2010	3688	WOCT6	14	44.97	4.07	5.69	12.11	0.20	32.15	0.06	20.40
10/30/2010	3708	WOCT6	14	41.84	5.15	7.13	17.16	0.17	27.23	4.42	18.47
12/11/2010	4179	WOCT6	14	42.46	6.48	6.29	14.13	0.10	47.57	3.07	20.10
1/19/2011	4250	WOCT6	14	16.83	4.28	4.11	10.33	0.13	13.56	3.51	7.20
2/19/2010	4374	WOCT6	14	27.53	4.31	2.69	7.34	0.15	14.81	2.14	9.97
3/25/2010	4452	WOCT6	14	18.43	6.26	6.27	18.76	0.19	25.47	0.06	24.10
5/17/2010	3412	WOCT7	15	25.07	11.41	7.31	13.96	0.19	31.39	3.84	46.17
6/2/2010	3495	WOCT7	15	42.63	9.96	13.93	26.78	0.25	53.49	1.36	82.51
6/24/2010	3556	WOCT7	15	41.89	10.93	9.81	22.85	0.27	41.06	0.57	47.81
7/23/2010	3604	WOCT7	15	32.47	11.98	12.11	23.42	0.22	37.72	5.27	51.35
12/11/2010	4177	WOCT7	15	29.07	17.21	9.81	19.64	0.17	39.80	4.97	25.78
2/19/2010	4373	WOCT7	15	31.01	7.01	4.83	12.06	0.05	23.72	3.04	15.12
3/25/2010	4459	WOCT7	15	53.10	15.95	14.58	29.33	0.16	60.16	0.34	67.58
5/17/2010	3413	WOCT8	16	44.31	8.54	11.84	23.95	0.18	52.66	2.71	82.98
6/2/2010	3496	WOCT8	16	80.57	7.99	15.36	25.06	0.28	74.54	0.93	103.83
6/24/2010	3549	WOCT8	16	51.26	6.11	12.91	26.59	0.19	48.02	0.50	107.13
7/23/2010	3590	WOCT8	16	61.61	9.72	18.10	30.91	0.25	70.97	4.60	119.08
9/26/2010	3665	WOCT8	16	55.96	5.10	9.13	14.42	0.41	46.51	0.15	98.35
10/9/2010	3684	WOCT8	16	77.96	7.73	14.44	23.57	0.38	61.53	0.80	262.30
10/30/2010	3713	WOCT8	16	37.67	8.43	7.26	15.69	0.21	31.21	0.14	44.17

12/11/2010	4184	WOCT8	16	39.01	11.28	12.70	21.44	0.08	43.52	4.56	60.67
1/19/2011	4251	WOCT8	16	24.13	8.40	6.52	13.67	0.10	26.99	5.27	45.49
2/19/2010	4372	WOCT8	16	52.62	10.86	10.39	19.36	0.03	56.71	4.34	56.92
3/25/2010	4463	WOCT8	16	64.50	11.56	16.62	35.27	0.24	72.43	5.92	78.83
5/17/2010	3414	WOCT9	17	30.23	5.06	5.02	12.91	0.12	23.45	0.59	20.15
6/2/2010	3497	WOCT9	17	20.53	6.31	6.53	15.83	0.10	20.30	0.23	23.48
6/24/2010	3553	WOCT9	17	36.16	4.96	6.62	19.86	0.26	31.68	0.94	43.77
7/23/2010	3599	WOCT9	17	29.10	7.35	7.51	20.99	0.13	34.25	4.86	26.47
9/26/2010	3657	WOCT9	17	81.33	7.04	3.89	10.74	0.57	49.32	2.60	105.90
10/30/2010	3712	WOCT9	17	23.24	6.03	3.73	10.54	0.18	13.58	1.54	20.22
12/11/2010	4188	WOCT9	17	73.47	12.66	9.08	25.62	0.52	48.54	9.79	104.87
1/19/2011	4252	WOCT9	17	27.35	9.69	5.83	16.57	0.13	26.85	4.72	37.71
2/19/2010	4365	WOCT9	17	44.06	7.19	6.24	18.42	0.15	33.59	5.29	38.94
3/25/2010	4462	WOCT9	17	45.51	8.21	9.76	25.43	0.31	39.60	0.22	48.78
5/17/2010	3409	WOCT2	18	36.32	8.00	9.07	36.90	0.54	39.12	6.90	74.25
6/2/2010	3492	WOCT2	18	6.92	4.35	2.62	7.41	0.11	6.69	1.04	11.63
6/24/2010	3563	WOCT2	18	33.51	8.07	7.15	31.55	0.71	24.04	7.51	33.24
9/26/2010	3658	WOCT2	18	24.61	3.97	1.57	9.04	0.16	13.92	3.24	33.62
10/30/2010	3705	WOCT2	18	35.26	5.25	4.88	19.67	0.25	16.13	6.66	25.80
12/11/2010	4186	WOCT2	18	22.98	7.78	6.59	25.35	0.16	16.48	4.77	39.16
1/19/2011	4247	WOCT2	18	12.24	6.03	4.49	18.33	0.22	23.37	4.99	26.33
2/19/2010	4367	WOCT2	18	62.75	8.22	9.30	32.07	0.82	48.15	9.12	81.69
3/25/2010	4455	WOCT2	18	55.50	10.58	13.41	58.05	0.67	50.28	4.78	108.45

Appendix 3 Raw data for subcatchments.

Date	NAWA ID	Sample ID	Creek #	DOC	TDN	DON	DON:TDN	DO	TS	TDS	TSS	Turbidity
					mg/L				mg/L			NU
4/5/2010	3372	Crosstimber	1	10.00	0.74	0.56	0.76					
5/17/2010	3423	Crosstimber	1	11.75	1.27	0.68	0.54					
6/2/2010	3502	Crosstimber	1	10.40	1.12	0.70	0.62		280	229	51	23
6/24/2010	3562	Crosstimber	1	11.10	1.17	0.69	0.59		154	92	62	13
7/23/2010	3593	Crosstimber	1	10.42	0.95	0.68	0.72					
9/26/2010	3661	Crosstimber	1	6.55	0.55	0.26	0.47	7.79	166	104	62	
10/30/2010		Crosstimber	1	18.58	0.68	0.58	0.84	5.10	240	125	115	30
1/19/2011	4249	Crosstimber	1	20.53	1.04	0.91	0.87	7.93	268	249	19	26
2/19/2011	4373	Crosstimber	1	17.31	0.97	0.84	0.86	7.06	774	753	21	23
3/25/2011	4456	Crosstimber	1	20.96	1.13	0.95	0.84	8.79	196	177	19	9
4/5/2010	3374	Lewis	2	12.11	0.68	0.39	0.57					
5/17/2010	3424	Lewis	2	12.94	1.11	0.58	0.52					
6/2/2010	3503	Lewis	2	13.62	1.05	0.49	0.46		320	287	33	4
6/24/2010	3558	Lewis	2	12.83	0.79	0.46	0.57		208	122	86	4
7/23/2010	3595	Lewis	2	16.12	1.17	0.77	0.66					
1/19/2011	4254	Lewis	2	15.93	0.64	0.52	0.81	7.05	256	240	16	16
3/25/2011	4460	Lewis	2	19.06	0.84	0.63	0.75	8.61	222	159	63	18
4/5/2010	3373	Piney	3	7.95	0.48	0.37	0.77					
5/17/2010	3422	Piney	3	6.30	0.59	0.31	0.53					
6/2/2010	3504	Piney	3	8.24	0.73	0.37	0.50		464	421	43	2
6/24/2010	3552	Piney	3	5.52	0.39	0.20	0.52		204	155	49	4
7/23/2010	3596	Piney	3	6.47	0.69	0.26	0.38					
10/9/2010	3689	Piney	3	6.74	0.39	0.22	0.57	6.28	162	148	14	
10/30/2010	3719	Piney	3	7.13	0.30	0.20	0.66	8.14	336	246	90	16
12/11/2010	4189	Piney	3	9.05	0.39	0.26	0.67	7.83	322	276	46	6
1/19/2011	4255	Piney	3	8.16	0.55	0.27	0.49	8.48	294	271	23	17
2/19/2011	4366	Piney	3	6.08	0.47	0.29	0.61	8.37	1294	1285	9	5
3/25/2011	4465	Piney	3	8.23	0.38	0.21	0.56	9.08	602	530	72	15
6/2/2010	3505	Ripley	4	9.80	0.87	0.46	0.53		532	413	119	12
6/24/2010	3550	Ripley	4	8.82	0.77	0.40	0.52		476	329	147	15
7/23/2010	3594	Ripley	4	10.35	0.71	0.44	0.61					
9/26/2010	3660	Ripley	4	7.06	0.49	0.25	0.50	8.59	440	328	112	
10/9/2010	3680	Ripley	4	8.36	0.55	0.35	0.64	7.37	194	135	59	

10/30/2010	3717	Ripley	4	8.12	0.56	0.32	0.57	8.30	260	183	77	50
12/11/2010	4176	Ripley	4	12.52	0.72	0.59	0.82	6.81	348	270	78	39
1/19/2011	4260	Ripley	4	10.07	0.58	0.33	0.57	7.77	300	248	52	42
3/25/2011	4461	Ripley	4	12.35	0.61	0.43	0.70	9.30	390	377	13	11
4/5/2010	3361	WOCT1	8	12.49	0.91	0.57	0.63					
5/17/2010	3408	WOCT1	8	8.71	1.03	0.39	0.38					
6/24/2010	3554	WOCT1	8	5.75	0.59	0.29	0.48		284	227	57	7
6/2/2010	3491	WOCT1	8	7.89	0.76	0.33	0.44		270	255	15	9
7/23/2010	3601	WOCT1	8	7.71	0.73	0.35	0.48					
9/26/2010	3662	WOCT1	8	5.23	0.44	0.21	0.48	8.56	186	139	47	
10/9/2010	3685	WOCT1	8	6.85	0.61	0.31	0.50	6.03	66		118	
10/30/2010	3714	WOCT1	8	9.93	0.69	0.47	0.68	7.67	216	59	157	39
12/11/2010	4175	WOCT1	8	9.86	0.49	0.40	0.81	6.85	222	165	57	36
1/19/2011	4246	WOCT1	8	9.96	0.58	0.37	0.64	7.70	256	204	52	38
2/19/2010	4370	WOCT1	8	11.85	0.68	0.56	0.82	6.85	2452	2424	28	30
3/25/2010	4458	WOCT1	8	15.65	0.87	0.68	0.79	8.37	174	158	16	9
5/17/2010	3415	WOCT10	9	10.44	0.89	0.43	0.48					
6/2/2010	3498	WOCT10	9	8.59	0.63	0.36	0.57		204	155	49	2
6/24/2010	3547	WOCT10	9	5.28	0.58	0.17	0.30		20	18	2	2
7/23/2010	3591	WOCT10	9	7.29	0.60	0.27	0.45					
9/26/2010	3667	WOCT10	9	9.14	0.68	0.24	0.35	7.80	148	113	35	
10/30/2010	3710	WOCT10	9	8.71	0.30	0.19	0.65	7.06	240	176	64	31
1/19/2011	4253	WOCT10	9	16.37	0.86	0.67	0.78	7.91	196	157	39	35
5/17/2010	3416	WOCT12	10	8.49	1.25	0.29	0.23					
6/2/2010	3499	WOCT12	10	6.97	0.97	0.18	0.19		234	207	27	3
6/24/2010	3564	WOCT12	10	6.95	0.96	0.25	0.26		226	139	87	4
7/23/2010	3603	WOCT12	10	6.37	0.82	0.24	0.29					
9/26/2010	3670	WOCT12	10	3.13	0.29	0.04	0.13	8.85	154	83	71	
10/9/2010	3681	WOCT12	10	3.65	0.44	0.05	0.10	6.65	21	0	21	
10/30/2010	3716	WOCT12	10	6.24	0.44	0.15	0.35	8.45	162	159	3	6
12/11/2010	4178	WOCT12	10	5.39	0.49	0.08	0.15	6.60	178	149	29	3
1/19/2011	4259	WOCT12	10	8.61	0.80	0.26	0.33	8.16	266	258	8	9
2/19/2010	4368	WOCT12	10	6.11	0.53	0.22	0.42	8.35	240	237	3	6
3/25/2010	4464	WOCT12	10	6.17	0.31	0.02	0.07	9.31	214	208	6	11
4/5/2010	3364	WOCT13	11	13.30	0.81	0.53	0.65					
5/17/2010	3417	WOCT13	11	7.48	0.82	0.29	0.35					
6/2/2010	3500	WOCT13	11	10.46	0.78	0.39	0.49		328	247	81	4

6/24/2010	3548	WOCT13	11	6.21	0.59	0.26	0.45		320	191	129	4
7/23/2010	3589	WOCT13	11	7.14	0.66	0.31	0.46					
9/26/2010	3669	WOCT13	11	4.25	0.37	0.09	0.23	8.42	454	237	217	
10/9/2010	3682	WOCT13	11	7.91	0.79	0.51	0.64	7.13	360	299	61	
10/30/2010	3711	WOCT13	11	4.91	0.24	0.10	0.43	7.92	332	319	13	6
12/11/2010	4183	WOCT13	11	9.12	0.38	0.29	0.76	6.18	322	241	81	3
1/19/2011	4258	WOCT13	11	9.10	0.48	0.29	0.60	8.18	372	353	19	18
2/19/2010	4369	WOCT13	11	6.32	0.39	0.28	0.72	8.17	614	607	7	5
3/25/2010	4466	WOCT13	11	9.97	0.41	0.26	0.64	8.46				12
5/17/2010	3418	WOCT14	12	5.53	0.62	0.20	0.32					
6/2/2010	3501	WOCT14	12	5.31	0.58	0.17	0.29		280	246	34	4
6/24/2010	3559	WOCT14	12	5.76	0.80	0.33	0.41		170	133	37	11
7/23/2010	3600	WOCT14	12	6.17	0.58	0.27	0.47					
9/26/2010	3666	WOCT14	12	3.23	0.29	0.12	0.40	8.45	342	266	76	
10/9/2010	3691	WOCT14	12	2.82	0.27	0.04	0.14	6.58	56	3	53	
10/30/2010	3704	WOCT14	12	8.70	0.64	0.44	0.68	7.98	186	121	65	23
12/11/2010	4180	WOCT14	12	6.36	0.54	0.14	0.25	7.30	242	204	38	8
1/19/2011	4257	WOCT14	12	9.80	0.74	0.28	0.38	8.22	296	280	16	19
2/19/2010	4376	WOCT14	12	5.95	0.50	0.25	0.50	8.34	308	301	7	11
3/25/2010	4453	WOCT14	12	6.70	0.30	0.08	0.26	9.52	306	294	12	12
4/5/2010	3362	WOCT3	13	12.24	1.00	0.57	0.57					
5/17/2010	3410	WOCT3	13	13.54	1.13	0.63	0.56					
6/2/2010	3493	WOCT3	13	12.96	0.87	0.57	0.65		274	189	85	2
6/24/2010	3557	WOCT3	13	12.47	0.66	0.51	0.77		296	171	125	7
7/23/2010	3597	WOCT3	13	12.40	0.82	0.62	0.75					
9/26/2010	3664	WOCT3	13	8.87	0.81	0.47	0.58	6.73	328	261	67	
10/9/2010	3687	WOCT3	13	7.86	0.50	0.32	0.63	6.99	526	410	116	
10/30/2010	3715	WOCT3	13	11.20	1.74	0.25	0.14	8.39	164	103	61	42
12/11/2010	4187	WOCT3	13	17.49	0.87	0.76	0.87	6.39	180	94	86	6
1/19/2011	4248	WOCT3	13	21.87	1.23	0.98	0.80	7.80	268	214	54	38
2/19/2010	4379	WOCT3	13	16.63	1.04	0.79	0.76	7.61	6200	6178	22	27
4/5/2010	3363	WOCT6	14	13.19	0.89	0.59	0.66					
5/17/2010	3411	WOCT6	14	10.97	0.74	0.42	0.56					
6/2/2010	3494	WOCT6	14	9.70	0.66	0.00	0.01		248	201	47	5
6/24/2010	3551	WOCT6	14	6.77	0.43	0.30	0.70		37	0	37	7
7/23/2010	3598	WOCT6	14	11.15	0.69	0.50	0.72					
9/26/2010	3664/3659	WOCT6	14	6.32	0.46	0.22	0.47	8.51	288	213	75	

10/9/2010	3688	WOCT6	14	7.91	0.76	0.20	0.26	6.49	142	88	54	
10/30/2010	3708	WOCT6	14	9.68	0.55	0.37	0.68	7.46	196	155	41	19
12/11/2010	4179	WOCT6	14	15.05	0.83	0.53	0.63	6.24	272	225	47	9
1/19/2011	4250	WOCT6	14	15.10	0.60	0.44	0.73	7.49	254	204	50	45
2/19/2010	4374	WOCT6	14	13.93	0.79	0.65	0.82	7.31	4782	4745	37	40
3/25/2010	4452	WOCT6	14	18.18	0.94	0.69	0.73	8.32	190	164	26	15
5/17/2010	3412	WOCT7	15	12.91	1.96	0.73	0.37					
6/2/2010	3495	WOCT7	15	11.48	1.15	0.56	0.49		686			
6/24/2010	3556	WOCT7	15	11.61	1.03	0.64	0.62					
7/23/2010	3604	WOCT7	15	12.42	0.98	0.70	0.71					
12/11/2010	4177	WOCT7	15	15.87	0.88	0.76	0.87	6.77	308			8
2/19/2010	4373	WOCT7	15	10.59	2.09	0.66	0.31	8.13				16
3/25/2010	4459	WOCT7	15	16.96	1.51	1.02	0.68	8.81				99
5/17/2010	3413	WOCT8	16	10.20	1.36	0.46	0.34					
6/2/2010	3496	WOCT8	16	10.83	0.96	0.56	0.58		476	376	100	4
6/24/2010	3549	WOCT8	16	7.96	0.74	0.40	0.54		518	295	223	5
7/23/2010	3590	WOCT8	16	12.03	0.94	0.63	0.67					
9/26/2010	3665	WOCT8	16	7.54	0.68	0.20	0.29	8.20	514	300	214	
10/9/2010	3684	WOCT8	16	10.30	0.92	0.43	0.47	7.03	364	338	26	
10/30/2010	3713	WOCT8	16	7.97	0.58	0.33	0.57	8.49	236	189	47	35
12/11/2010	4184	WOCT8	16	16.40	0.86	0.74	0.86	6.21	328	226	102	5
1/19/2011	4251	WOCT8	16	13.44	1.94	0.60	0.31	7.73	350	267	83	66
2/19/2010	4372	WOCT8	16	12.51	1.60	0.65	0.41	8.05	6174	6162	12	17
3/25/2010	4463	WOCT8	16	13.70	0.77	0.59	0.77	9.77	420	401	19	8
5/17/2010	3414	WOCT9	17	12.58	0.91	0.52	0.57					
6/2/2010	3497	WOCT9	17	10.93	0.63	0.45	0.71		320	241	79	7
6/24/2010	3553	WOCT9	17	7.30	0.78	0.34	0.44		348	208	140	8
7/23/2010	3599	WOCT9	17	10.67	0.71	0.54	0.76					
9/26/2010	3657	WOCT9	17	6.89	1.29	0.15	0.12	8.46	404	311	93	
10/30/2010	3712	WOCT9	17	7.89	0.70	0.05	0.08	8.05	114	46	68	34
12/11/2010	4188	WOCT9	17	12.50	2.44	0.57	0.23	7.85	408	314	94	9
1/19/2011	4252	WOCT9	17	13.30	2.03	0.62	0.31	7.92	338	261	77	59
2/19/2010	4365	WOCT9	17	12.23	1.53	0.54	0.35	8.41	262	253	9	15
3/25/2010	4462	WOCT9	17	14.05	0.86	0.60	0.70	8.83	320	257	63	35
5/17/2010	3409	WOCT2	18	9.85	3.56	0.31	0.09					
6/2/2010	3492	WOCT2	18	7.90	0.76	0.35	0.45	7.59	444	376	68	12
6/24/2010	3563	WOCT2	18	9.23	0.64	0.51	0.79		254	146	108	4

9/26/2010	3658	WOCT2	18	7.04	2.23	0.21	0.09		244	104	140	
10/30/2010	3705	WOCT2	18	6.52	0.76	0.22	0.29	7.82	192	137	55	10
12/11/2010	4186	WOCT2	18	8.98	0.74	0.35	0.48	6.71	236	165	71	5
1/19/2011	4247	WOCT2	18	12.49	2.30	0.17	0.07	7.96	262	247	15	15
2/19/2010	4367	WOCT2	18	7.39	2.39	0.08	0.03	8.20	4646	4638	8	4
3/25/2010	4455	WOCT2	18	12.06	0.90	0.51	0.57	8.20	464	433	31	8

Appendix 4 Raw data for main stem sites nutrients and cations (mg/L)

Date	NAWA ID	Sample ID	Creek #	pH	EC	NH_4-N	NO_3-N	PO_4-P	$CaCO_3$	Na	K	Mg	Ca
					µS/cm	mg/L							
4/5/2010	3367	WOCMS1	5	7.27	340	0.18	0.26	0.06	40.14	19.80	6.28	7.95	13.78
5/17/2010	3419	WOCMS1	5	7.39		0.12	0.67	0.07	62.92	33.13	6.13	9.38	21.10
6/2/2010	3506	WOCMS1	5	7.1		0.12	0.68	0.05	51.22	25.49	5.80	7.20	15.50
6/24/2010	3561	WOCMS1	5	7.1	293	0.11	0.38	0.06	51.49	26.08	4.33	5.19	13.04
7/23/2010	3588	WOCMS1	5	7.2	390	0.09	0.34	0.04	61.94	33.14	5.97	6.67	16.20
9/26/2010	3662	WOCMS1	5	7.2	580	0.10	0.11	0.03	80.33	26.59	3.18	4.51	13.26
10/9/2010	3690	WOCMS1	5	7.6	470	0.08	0.13	0.04	89.24	33.98	3.10	5.14	12.27
10/30/2010	3707	WOCMS1	5	7.3	220	0.07	0.36	0.09	63.00	47.07	5.84	4.03	9.76
12/11/2010	4182	WOCMS1	5	7.3	250	0.07	0.10	0.06	22.00	23.11	6.32	6.74	14.77
1/19/2011	4256	WOCMS1	5	7.6	400	0.10	0.27	0.08	56.00	43.88	9.18	7.59	17.53
2/19/2011	7377	WOCMS1	5	6.7	280	0.11	0.45	0.10	79.00	51.34	6.09	6.04	15.90
3/25/2011	4467	WOCMS1	5	7	410	0.12	0.21	0.04	73.08	42.54	7.11	9.43	23.01
4/5/2010	3368	WOCMS2	6	7.21	490	0.17	0.58	0.06	33.19	27.95	6.80	8.81	16.43
5/17/2010	3420	WOCMS2	6	7.1	490	0.14	1.29	0.07	56.67	41.36	6.88	10.22	22.54
6/2/2010	3507	WOCMS2	6	7.2	388	0.12	1.01	0.06	57.35	30.08	7.62	7.85	17.98
6/24/2010	3555	WOCMS2	6	7.1	416	0.12	0.49	0.04	66.61	39.04	6.26	7.78	17.80
7/23/2010	3592	WOCMS2	6	7.1	380	0.10	0.44	0.04	63.53	31.55	6.98	7.87	18.18
9/26/2010	3656	WOCMS2	6	7.7	590	0.14	0.14	0.05	93.20	60.90	5.87	4.80	7.80
10/9/2010	3683	WOCMS2	6	7.9	620	0.10	0.38	0.06	135.34	83.59	8.17	7.18	13.80
10/30/2010	3705	WOCMS2	6	7.2	300	0.07	1.51	0.25	43.00	48.54	7.22	4.73	13.06
12/11/2010	4185	WOCMS2	6	7.4	320	0.06	0.07	0.07	70.00	32.18	7.87	7.28	20.33
1/19/2011	4261	WOCMS2	6	7.6	320	0.10	0.48	0.31	51.00	19.93	9.33	5.36	15.57
2/19/2011	4371	WOCMS2	6	6.9	260	0.14	0.54	0.10	43.00	26.47	6.75	5.90	16.18
3/25/2011	4454	WOCMS2	6	6.9	420	0.15	0.32	0.12	84.14	46.28	8.45	10.19	25.80
4/5/2010	3369	WOCMS4	7	7.09	280	0.22	0.13	0.04	46.74	12.91	8.05	5.93	11.34

5/17/2010	3421	WOCMS4	7	7.4		0.12	4.24	0.49	55.53	42.08	10.68	8.05	20.22
6/2/2010	3508	WOCMS4	7	7.2	520	0.09	4.50	0.40	65.54	50.42	9.00	8.25	22.83
6/24/2010	3560	WOCMS4	7	7.5	669	0.09	6.38	0.26	82.79	75.63	10.59	11.12	26.06
7/23/2010	3602	WOCMS4	7	7.3	690	0.11	5.24	0.43	96.73	64.74	10.78	8.21	26.30
9/26/2010	3663	WOCMS4	7	7.9	740	0.08	2.23	1.16	85.78	44.34	4.97	2.90	14.89
10/9/2010	3686	WOCMS4	7	7.5	690	0.09	6.71	0.91	109.97	96.47	9.89	5.71	22.99
10/30/2010	3709	WOCMS4	7	7.2	210	0.06	1.17	0.27	55.00	36.49	5.60	3.53	11.62
12/11/2010	4181	WOCMS4	7	7.4	540	0.06	3.02	0.37	103.00	46.77	9.33	6.42	21.26
1/19/2011	4262	WOCMS4	7	7.9	240	0.24	0.98	0.03	26.00	25.42	5.22	7.69	16.48
2/19/2011	4378	WOCMS4	7	6.9	530	0.09	1.84	0.20	97.00	68.30	8.08	6.81	19.88
3/25/2011	4457	WOCMS4	7	7.4	680	0.17	0.65	0.34	129.58	75.72	12.57	10.24	35.09

Appendix 5 Raw data for main stem anions and ratios.

Date	NAWA ID	Sample ID	Creek #	F^-	Cl^-	NO_3^-	SO_4^{2-}	NPOC	TN	CNP ratio	DON	DON:TDN Ratio
				mg/L							mg/L	
4/5/2010	3367	WOCMS1	5	0.18	25.57	0.53	32.90	11.32	0.90	215.16	0.47	0.52
5/17/2010	3419	WOCMS1	5	0.17	43.61	2.38	55.89	10.44	1.26	124.17	0.46	0.37
6/2/2010	3506	WOCMS1	5	0.22	34.09	2.14	32.46	9.47	1.21	149.00	0.41	0.34
6/24/2010	3561	WOCMS1	5	0.14	23.65	1.10	26.15	8.52	0.87	176.63	0.37	0.43
7/23/2010	3588	WOCMS1	5	0.16	35.46	4.40	38.00	7.86	0.76	230.78	0.33	0.43
9/26/2010	3662/3668	WOCMS1	5	0.14	23.18	0.08	53.48	5.17	0.40	441.40	0.19	0.47
10/9/2010	3690	WOCMS1	5	0.26	27.11	0.07	57.89	4.72	0.35	348.94	0.13	0.38
10/30/2010	3707	WOCMS1	5	0.13	23.63	3.67	28.55	6.34	0.61	115.48	0.18	0.30
12/11/2010	4182	WOCMS1	5	0.15	23.36	3.29	34.77	8.50	0.53	267.30	0.35	0.67
1/19/2011	4256	WOCMS1	5	0.06	37.49	4.28	61.06	11.06	0.87	158.91	0.50	0.57
2/19/2011	7377	WOCMS1	5	0.05	37.48	2.21	52.82	9.54	0.95	104.17	0.39	0.41
3/25/2011	4467	WOCMS1	5	0.34	46.63	0.41	67.95	11.99	0.72	384.79	0.39	0.54
4/5/2010	3368	WOCMS2	6	0.23	35.66	1.53	55.82	10.95	1.27	151.89	0.52	0.41
5/17/2010	3420	WOCMS2	6	0.20	44.18	4.45	74.74	10.69	1.83	78.63	0.40	0.22
6/2/2010	3507	WOCMS2	6	0.25	33.31	3.62	46.05	10.89	1.69	103.44	0.56	0.33
6/24/2010	3555	WOCMS2	6	0.18	34.71	1.50	51.79	7.86	0.98	192.00	0.37	0.38
7/23/2010	3592	WOCMS2	6	0.30	29.90	5.01	44.56	8.18	0.85	213.33	0.31	0.36
9/26/2010	3656	WOCMS2	6	0.28	42.88	0.28	83.21	6.91	0.50	294.99	0.22	0.44
10/9/2010	3683	WOCMS2	6	0.55	58.76	0.94	154.17	7.60	0.81	164.02	0.33	0.40
10/30/2010	3705	WOCMS2	6	0.14	27.14	12.59	38.63	5.34	1.24	17.23		0.00
12/11/2010	4185	WOCMS2	6	0.12	25.66	3.58	50.70	10.56	0.64	234.98	0.51	0.80
1/19/2011	4261	WOCMS2	6	0.15	19.34	4.60	35.33	12.33	1.14	34.98	0.56	0.49
2/19/2011	4371	WOCMS2	6	0.18	24.09	3.58	41.30	12.05	1.23	97.64	0.55	0.45
3/25/2011	4454	WOCMS2	6	0.17	38.43	4.22	57.93	13.73	1.01	111.34	0.54	0.54
4/5/2010	3369	WOCMS4	7	0.14	20.73	0.39	26.99	13.10	1.01	314.91	0.66	0.65

5/17/2010	3421	WOCMS4	7	0.20	44.48	14.31	56.64	13.55	5.02	5.50	0.66	0.13
6/2/2010	3508	WOCMS4	7	0.31	49.05	19.30	71.10	9.28	5.45	4.23	0.85	0.16
6/24/2010	3560	WOCMS4	7	0.36	71.82	27.34	104.03	10.16	6.88	5.71	0.40	0.06
7/23/2010	3602	WOCMS4	7	0.46	60.19	21.22	71.70	8.51	5.25	3.77	0.00	0.00
9/26/2010	3663	WOCMS4	7	0.65	27.79	6.72	89.77	5.56	2.36	2.04	0.05	0.02
10/9/2010	3686	WOCMS4	7	0.37	66.87	29.30	198.82	8.06	7.07	1.25	0.27	0.04
10/30/2010	3709	WOCMS4	7	0.21	18.54	8.04	23.76	8.63	1.46	21.89	0.23	0.16
12/11/2010	4181	WOCMS4	7	0.28	35.49	9.93	69.25	9.03	2.94	8.30		
1/19/2011	4262	WOCMS4	7		24.69	2.41	64.39	12.40	1.68	246.03	0.46	0.27
2/19/2011	4378	WOCMS4	7	0.06	49.13	3.49	74.66	9.65	2.37	20.37	0.44	0.19
3/25/2011	4457	WOCMS4	7	0.37	53.92	6.87	85.18	14.15	1.56	27.03	0.74	0.47

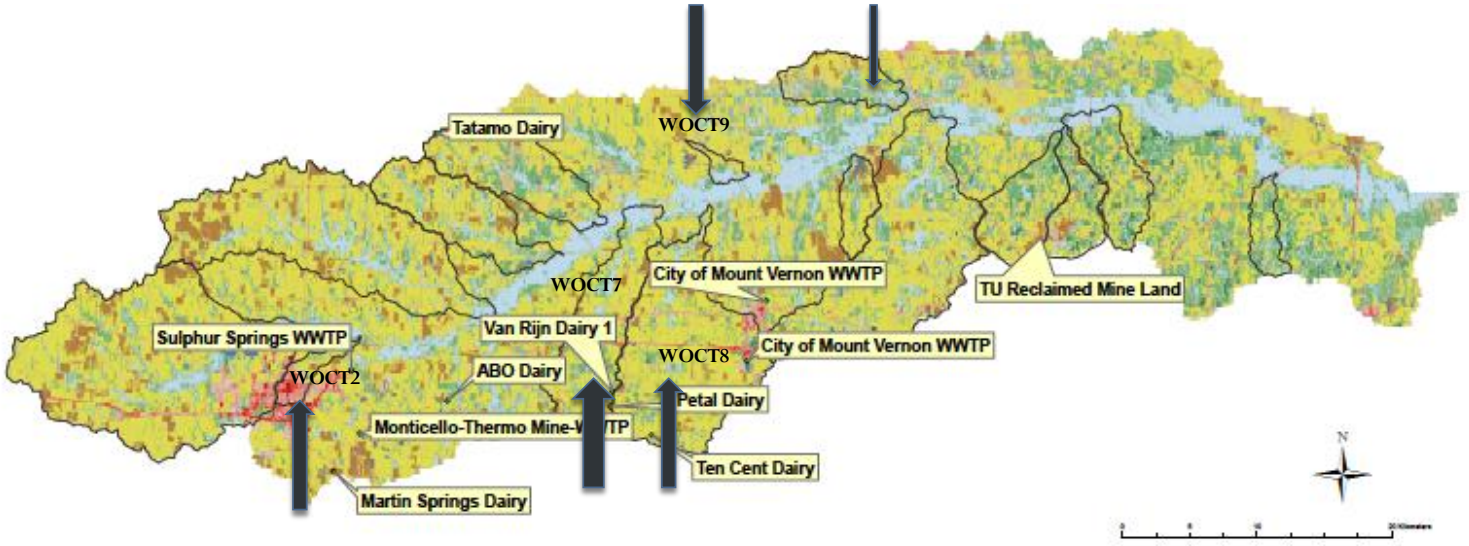
Appendix 6 Raw data for dissolved oxygen and solids in the main stem

Date	NAWA ID	Sample ID	Creek #	DO	TS	TDS	TSS	Turbidity
4/5/2010	3367	WOCMS1	5					
5/17/2010	3419	WOCMS1	5					
6/2/2010	3506	WOCMS1	5		344	274	70	8.85
6/24/2010	3561	WOCMS1	5		202	193	9	10.20
7/23/2010	3588	WOCMS1	5					
9/26/2010	3662/3668	WOCMS1	5	8.71	368	201	167	
10/9/2010	3690	WOCMS1	5	7.07	138	107	31	
10/30/2010	3707	WOCMS1	5	8.28	310	177	133	69.80
12/11/2010	4182	WOCMS1	5	7.39	218	151	67	25.90
1/19/2011	4256	WOCMS1	5	7.98	1020	966	54	38.00
2/19/2011	7377	WOCMS1	5	8.42	230	204	26	28.50
3/25/2011	4467	WOCMS1	5	9.33	336	264	72	41.70
4/5/2010	3368	WOCMS2	6					
5/17/2010	3420	WOCMS2	6					
6/2/2010	3507	WOCMS2	6		258	217	41	8.10
6/24/2010	3555	WOCMS2	6		262	162	100	4.80
7/23/2010	3592	WOCMS2	6					
9/26/2010	3656	WOCMS2	6	8.81	352	206	146	
10/9/2010	3683	WOCMS2	6	6.49	216	195	21	
10/30/2010	3705	WOCMS2	6	7.43	288	233	55	39.80
12/11/2010	4185	WOCMS2	6	7.52	240	211	29	13.00
1/19/2011	4261	WOCMS2	6	7.83	346	253	93	50.10
2/19/2011	4371	WOCMS2	6	8.26	252	240	12	23.70
3/25/2011	4454	WOCMS2	6	9.33	306	304	2	25.70
4/5/2010	3369	WOCMS4	7					
5/17/2010	3421	WOCMS4	7					

6/2/2010	3508	WOCMS4	7		412	309	103	8.70
6/24/2010	3560	WOCMS4	7		476	260	216	9.32
7/23/2010	3602	WOCMS4	7					
9/26/2010	3663	WOCMS4	7	8.93	474	281	193	
10/9/2010	3686	WOCMS4	7	6.96	300	237	63	
10/30/2010	3709	WOCMS4	7	7.81	194	124	70	33.00
12/11/2010	4181	WOCMS4	7	7.70	356	252	104	3.85
1/19/2011	4262	WOCMS4	7	7.72	280	232	48	40.20
2/19/2011	4378	WOCMS4	7	8.35	7552	7545	7	8.50
3/25/2011	4457	WOCMS4	7	9.29	438	399	39	16.20

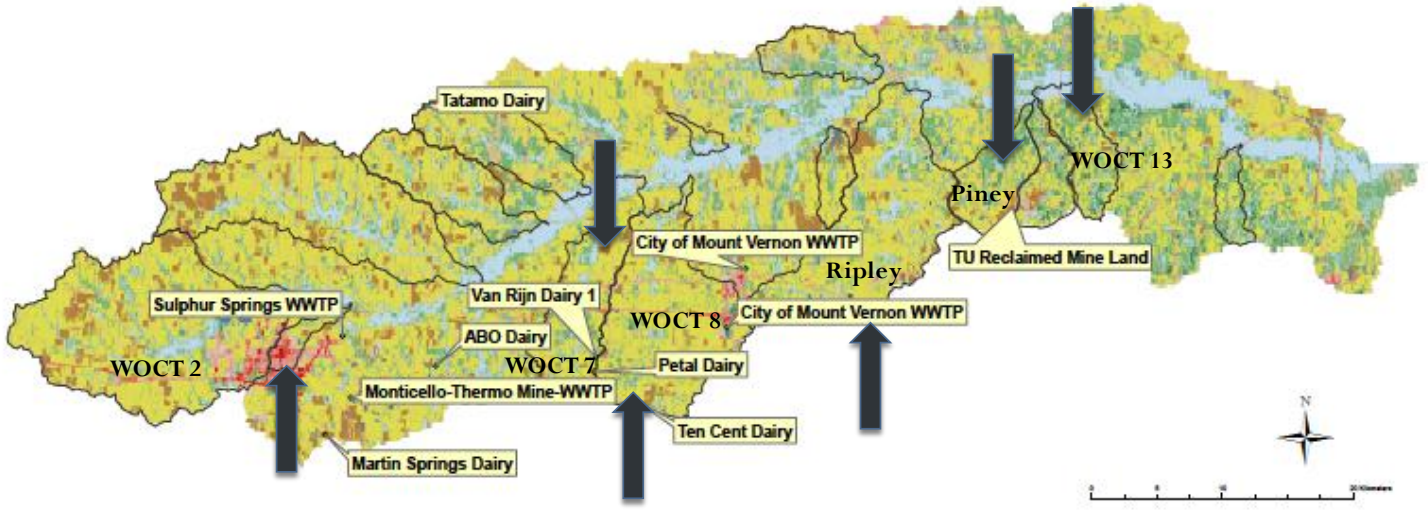
Appendix 7. Subcatchment land use and nitrogen and phosphorus.

NH_4^+-N	NO_3^-N	PO_4^{3-}P
• Correlation: Urban (+)	• Correlation: Deciduous Forest (-)	• Correlation: Pasture (+), Deciduous Forest (-)
• Sub-catchments: WOCT2, WOCT8, Lewis	• Sub-catchments: WOCT2, WOCT7, WOCT9	• Sub-catchments: WOCT2 & WOCT7
• Source: Fertilizer, manure, WWTP, urban runoff	• Source: fertilizer, manure, sewage effluent, dairy discharge	• Source: Timber harvest, dairy discharge, manure, sewage effluent



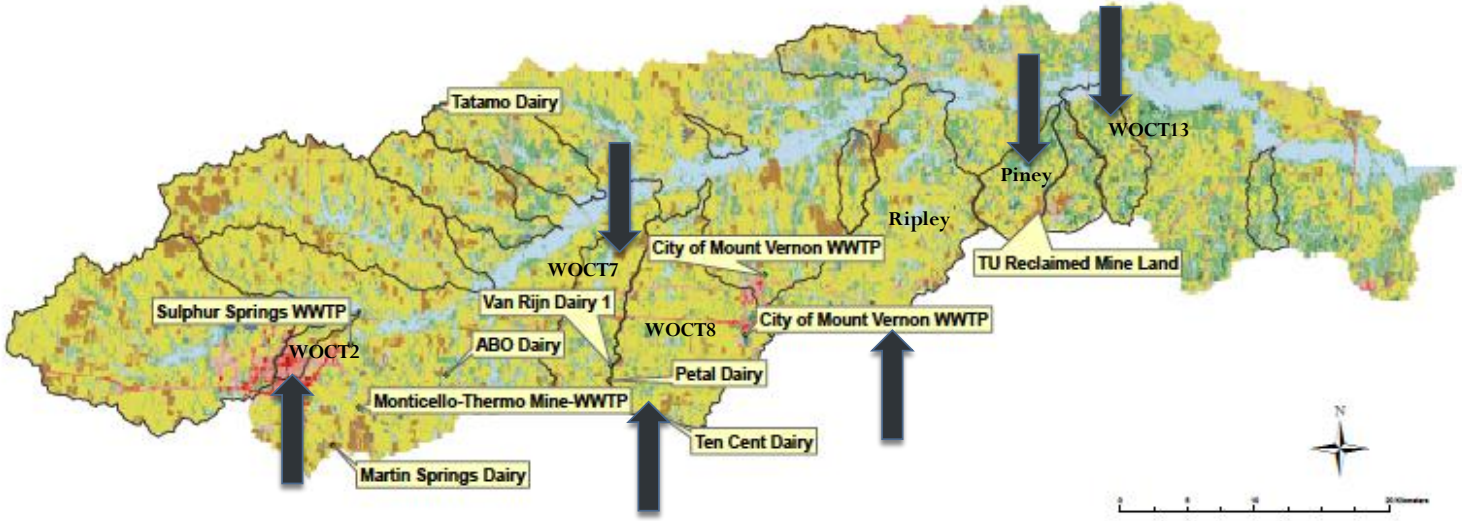
Appendix 8. Subcatchment land use and cations

Na^+	K^+	Ca^{2+}	Mg^{2+}
• Correlation: None • Sub-catchments: WOCT8, WOCT13, Ripley, Piney • Source: Bedrock, wastewater effluent, NaOH water treatment	• Correlation: None • Sub-catchments: WOCT7, WOCT8 • Source: Fertilizer, timber harvest, Potassium alum water treatment	• Correlation: Urban (+), Open water (-) • Sub-catchments: WOCT2, WOCT8, WOCT13, Piney • Source: Bedrock, urban runoff	• Correlation: Urban (+) • Sub-catchments: WOCT8, WOCT13, Piney • Source: Bedrock



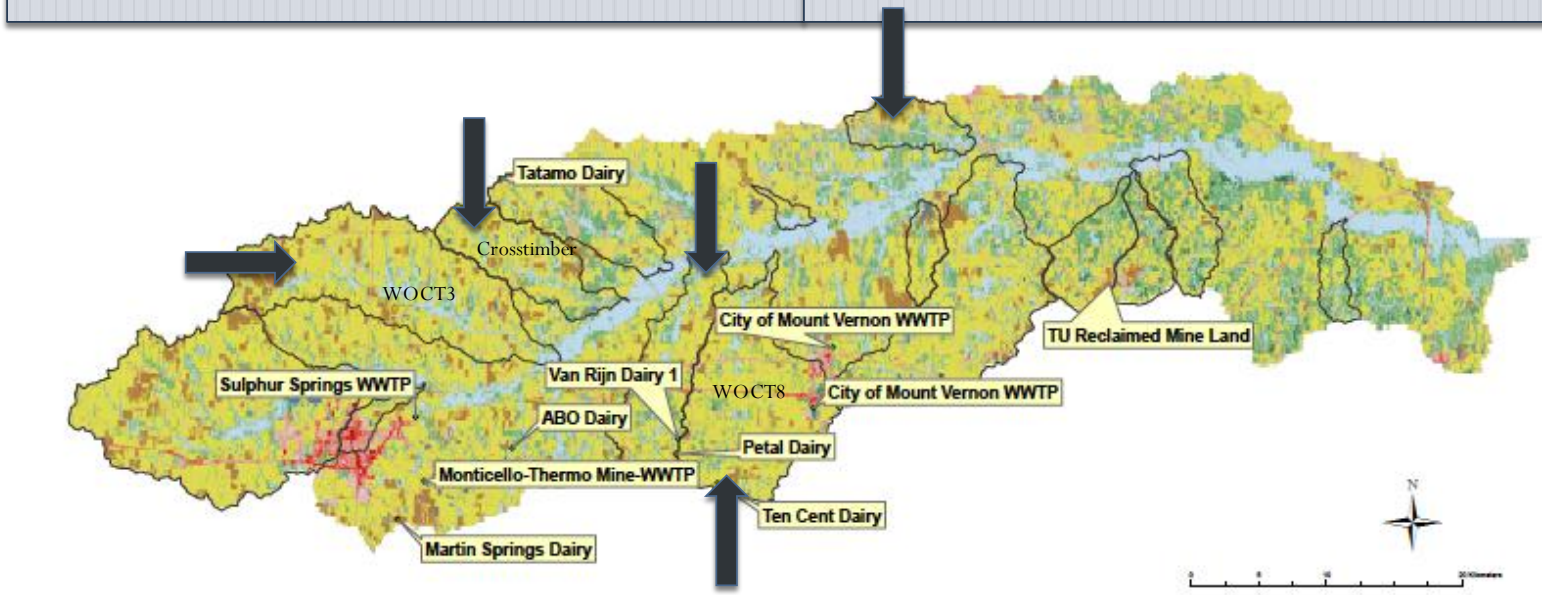
Appendix 9. Subcatchment land use and anions

F^-	Cl^-	SO_4^{2-}
• Correlation: Cultivated Crop (-)	• Correlation: Evergreen Forest(+). Open water (-)	• Correlation: Deciduous and Evergreen Forest (-)
• Sub-catchments: WOCT2	• Sub-catchments: WOCT8, WOCT7, WOCT6, WOCT14, WOCT13, Ripley, Piney Lewis	• Sub-catchments: Piney, WOCT8, WOCT13, Ripley
• Source: Fluoride additions to water supply	• Source: Bedrock, treated water, septic systems	• Source: Iron pyrite, coal, sodium sulfate



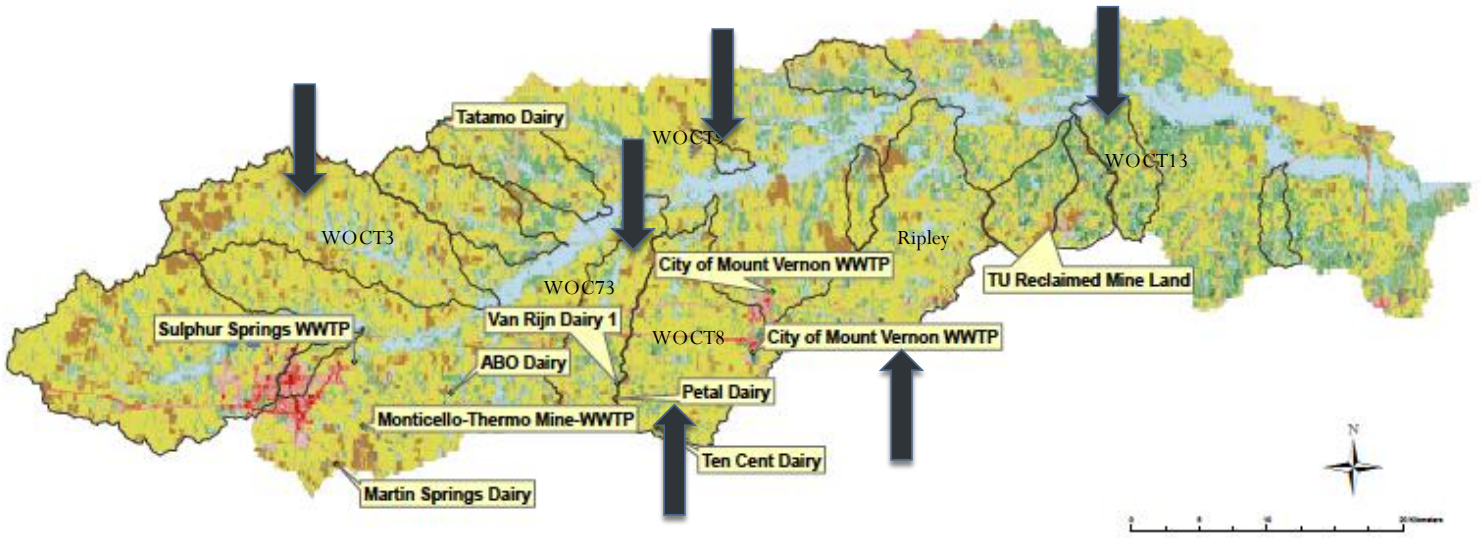
Appendix 10 Subcatchment landuse and DOC and DON

- DOC
  - Correlation: Urban (+), Deciduous and Evergreen Forest (-)
  - Sub-catchments: Lewis, Crosstimber, WOCT3, WOCT7, WOCT8
  - Source: WWTP, terrestrial
- DON
  - Correlation: Pasture (+), Barren land (-)
  - Sub-catchments: WOCT7, Crosstimber, Lewis, WOCT3, WOCT8
  - Source: manure, dairy discharge, terrestrial



Appendix 11. Subcatchment landuse and total suspended solids and turbidity

- **TSS**
  - Correlation: Pasture (+), Evergreen Forest (-)
  - Sub-catchments: WOCT8, WOCT9, Ripley, WOCT3, WOCT13
  - Source: Manure, Road dust, construction
- **Turbidity**
  - Correlation: Pasture (+), Evergreen Forest (-)
  - Sub-catchments: WOCT7, WOCT9, Ripley, WOCT1
  - Source: Manure, Construction, Road dust



VITA

Eliza Watson received her Bachelor of Arts degree in Peace and Conflict Studies and Human Rights from The Gallatin School of Individualized Study at New York University in 2005. After receiving her B.A. she worked for the International Rescue Committee where she worked in the Child and Youth Protection and Development Unit working on programs for international refugees and later as a consultant. Prior to entering the Water Management and Hydrological Science program at Texas A&M University in 2009, she spent time traveling extensively, volunteering in India, working on her family's ranch in Texas, and taking agricultural and science courses at Texas A&M –Commerce. As a Master of Science candidate at Texas A&M, she has focused her research on the impact of land use on surface water quality. She plans to follow a career in environmental management upon completing her degree.

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