

RELATIONSHIPS BETWEEN LANDSCAPE, SPATIAL SCALE,
AND STREAM WATER CHEMISTRY IN A
SUBTROPICAL KARST SYSTEM

THESIS

Presented to the Graduate Council of
Texas State University-San Marcos
in Partial Fulfillment
of the Requirements

for the Degree

Master of SCIENCE

by

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San Marcos, Texas
August 2009

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Jessica D. Strickland

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DEDICATION

I dedicate this thesis to my mother,

Without you, this and so many other things in my life would not have been possible

ACKNOWLEDGEMENTS

I would like to thank my family, friends, and Bance who have dealt with my stress, tears, and broken bones. I would especially like to thank my brother Jackson, whose love of animals is always an inspiration. I would also like to thank my office and lab mates that have helped me along the way, with a special thanks to Jesse Becker.

This thesis project was funded by The Nature Conservancy and several generous residents of the Pedernales River watershed. Last and certainly not least, I would like to give a special thanks to my committee who fully supported me in this process. I will always consider y'all dear friends and without you I would never have made it.

This manuscript was submitted on June 19, 2009.

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ABSTRACT

RELATIONSHIPS BETWEEN LANDSCAPE, SPATIAL SCALE, AND STREAM WATER CHEMISTRY IN A SUBTROPICAL KARST SYSTEM

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August 2009

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Natural factors such as climate, geology, topography, and vegetation regulate biogeochemical processes that dictate important river characteristics, including surface water chemistry (Allan, 2004). Converting natural vegetation for urban and agricultural land use can alter water chemistry, creating a loss of biodiversity and reduced human consumptive and recreational use (Osborne and Wiley, 1988; Johnson et al., 1997). To evaluate landscape-water chemistry interactions in a subtropical context, landscape characteristics (natural and anthropogenic) were quantified at three spatial scales (sub-

catchment, riparian, stream reach) and related to water chemistry variables collected over a 13-month sampling period. An additional dataset was incorporated into analysis to evaluate seasonal and long-term (1984-2008) temporal trends across contrasting stream flow conditions (low and high stream periods).

Landscape features accounted for slightly more variation in winter (52%) versus summer (48%) water chemistry (RDA, $P < 0.0001$). Nitrate ($\text{NO}_3\text{-N}$) concentrations were found to be highest in the winter, near headwater and agricultural stream reaches, and in higher stream flow. Riparian areas with forested vegetation and clayey soils were negatively associated with $\text{NO}_3\text{-N}$, which is consistent with terrestrial biological processes. Particulate substances (total phosphorus, chlorophyll *a*, and turbidity) were also associated with stream flow, clayey soils, and agricultural areas; however, concentrations were found to be highest during the summer in sub-catchments having steeper slopes and more urban land use. Specific conductivity and acid neutralizing capacity were highly correlated, and consistently negatively associated with sub-catchment urban land use and slope.

Seasonal temporal trends were found in most nutrient species, whereas long-term trends occurred only in $\text{NO}_3\text{-N}$, soluble reactive phosphorus (SRP), and organic nitrogen (ON). Seasonal trends were consistent with the data collected throughout the watershed during 2007 and 2008, particularly in relation to the differences found across discharge periods. Nitrate concentrations have increased from 1984 to 2008 across both flow regimes (low and high stream flow) (GLS: $\beta_1 = 1.06$, $P = 0.03$; $\beta_1 = 1.03$, $P = 0.02$), whereas ON has decreased during low flow conditions ($\beta_1 = -1.02$, $P = 0.04$).

Atmospheric $\text{NO}_3\text{-N}$ deposition did not increase over the data period ($t_{17} = -0.34$, $P = 0.74$), which suggests that N-related trends are associated with land cover change.

Soluble reactive P was highest (20 $\mu\text{g/L}$) in winter months characterized by low stream flows, which corresponded with the long-term increasing trend found only in the low flow period ($\beta_1 = 1.05$, $P = 0.03$). These data suggest that the stochastic flow regime of the study area exerts a large influence on stream water chemistry through the regulation of landscape-aquatic connectivity across multiple spatial and temporal scales.

CHAPTER 1

1. INTRODUCTION

Various aspects of river ecosystems are influenced by their terrestrial surroundings (Dodds, 1997) and riverine dynamics are increasingly evaluated from a landscape perspective (Allan, 2004). Natural features such as climate, geology, topography, and vegetation regulate biogeochemical processes that dictate important river characteristics, including surface water chemistry (Johnson et al., 1997). Terrestrial vegetation is particularly important in regulating nutritional resources, primarily in the input and retention of nutrients such as carbon (C), nitrogen (N) and phosphorus (P) (Gregory et al., 1991; Carpenter et al., 1998).

Human impacts, including converting vegetated areas to urban or agricultural use, alter primary pathways for nutrient inputs to rivers such as surface and subsurface flow, sediment transport, and atmospheric deposition (Osborne and Wiley, 1988; Johnson et al., 1997; Carpenter et al., 1998; Stewart et al., 2001). Negative implications of anthropogenic land use on stream integrity are well documented, particularly the effects of nutrient loading (Carpenter et al., 1998; Dodds and Welch, 2000). Since N and P are often the primary limiting nutrients in aquatic systems, increased loading of these nutrients can lead to changes in trophic state, loss of biodiversity, and impairment of human consumptive and recreational use (Allan and Flecker, 1993; Dodds, 2007; Dodds and Oakes, 2008).

Human activities have altered the N cycle through fertilizer application, cultivation of N-fixing crops, and burning of fossil fuels (Vitousek et al., 1997; Bernot and Dodds, 2005). These activities increase surface water dissolved inorganic N concentrations, which can modify natural biogeochemical processes (i.e., assimilation, denitrification, and sorption) that mediate downstream export (Bernot and Dodds, 2005; Arango and Tank, 2008; Herrman et al., 2008). Phosphorus often enters aquatic systems from agricultural landscapes in the particulate form during precipitation events, or as soluble reactive phosphorus (SRP) via urban wastewater effluent (Soranno et al., 1996; Carpenter et al., 1998). Urban areas not only alter the chemical composition of surface waters with wastewater effluent, but also through runoff from impervious surfaces (Lenat and Crawford, 1994; Paul and Meyer, 2001). Thus human activities are coupled with natural vegetation and topographic features that regulate biological and transport processes (Booth and Jackson, 1997; Paul and Meyer, 2001).

Landscape-aquatic interactions are a function of several pathways and processes that operate at multiple spatial scales, most commonly characterized in a nested hierarchy of physical units (i.e., habitat-reach-subcatchment-watershed) (Allan and Johnson, 1997). Particular emphasis has been placed on land use in the land-water interface (i.e., riparian corridor) due to the potential regulation of material transfer in surface runoff and groundwater (Karr and Schlosser, 1978; Gregory et al., 1991; Hill, 1996). Several studies have found that riparian land use is a better predictor of surface water chemistry (Osborne and Wiley, 1988; Johnson et al., 1997; Dodds and Oakes, 2008) compared to regional or catchment scale land use patterns (Jones et al., 2001; Sliva and Williams, 2001). However, contradictory results might be the product of topographic, geologic, or other

natural features, which are often excluded in watershed management studies (Sliva and Williams, 2001; Sabater et al., 2003; Allan, 2004). Thus, identifying important landscape-stream water chemistry relationships at multiple scales (i.e., catchment, riparian, and stream reach) across diverse geological and climatic conditions is needed to fully understand terrestrial influences on aquatic environments (Allan and Johnson, 1997; Townsend and Riley, 1999).

Several conceptual models of riverine nutrient dynamics, including the river continuum concept (Vannote et al., 1980), the flood pulse concept (Junk et al., 1989), autochthonous versus allochthonous loading model (Minshall, 1978), and the riverine productivity model (Thorpe and Delong, 1994) were created based on studies conducted in temperate latitudes (Dodds, 2002a). River ecosystem trophic state is largely controlled by landscape features including, canopy cover, external carbon source, nutrients, and hydrology, which are often highly dependent on latitude and longitude (Dodds, 2007). Applying generalized models across ecoregions can create misinterpretations of landscape-aquatic interactions (Dodds, 1997; Jones et al., 2001; Sabater et al., 2003), particularly when land use alone is quantified (Johnson et al., 1997; Sliva and Williams, 2001). While a relatively larger number of studies evaluating river systems have been conducted in north temperate forested zones (Dodds, 1997), the implications of land cover conversion in subtropical and tropical systems are less well known.

There were two main objectives of this study. The first objective was to evaluate the relationships between landscape features (natural and anthropogenic) and water chemistry in a subtropical karstic watershed. More specifically, I wanted to assess how human (land use) and natural (soil composition, geology, and topography) catchment

characteristics interact to influence water chemistry across season and multiple spatial scales (sub-catchment, riparian, stream reach). To compare the results of the first objective to long-term stream conditions, an additional dataset was incorporated into analysis. The available long-term dataset was used to achieve the second major objective, which was to evaluate temporal patterns (seasonal and long-term) in nutrient chemistry. To assess how stream discharge conditions influence long-term trends in nutrient composition, the data were evaluated under contrasting flow regimes (low and high-discharge conditions).

2. MATERIALS AND METHODS

2.1. STUDY AREA

This study was conducted in the Pedernales River watershed, a 3,300 km² drainage basin located in the eastern Edwards Plateau region of central Texas, USA. The 170 km perennial mainstem descends 396 m to the confluence with the Colorado River (LCRA, 2000) (Figure 1, subset). The climate of study area is characterized as subtropical-semiarid with an average annual temperature and precipitation of 19°C and 860 mm, respectively (Johnson City gauge; NCDC, 2002). The annual precipitation curve exhibits a bi-modal regime, with distinct peaks in May and October (125 and 101 mm, respectively) (NCDC, 2002). Major urban areas within the watershed are the cities of Fredericksburg (population 8,911), and Johnson City (1,191) (USCB, 2000).

The Edwards Plateau ecoregion overlies the Edwards-Trinity Aquifer, a 108,780-km² karstic aquifer system, largely dominated by Cretaceous-aged limestone rock formed

from marine deposits (Barker and Ardis, 1996). The carbonate-rich limestone rock provides a unique ionic aspect to surface water chemistry, ultimately leading to high acid neutralizing capacity (Groeger and Gustafson, 1994; Cave and Groeger, 2007). The hydrogeology of the study area is described as having conduit groundwater-surface water connectivity, thus base flows and headwater reaches receive groundwater through fault or fissure springs (Barker and Ardis, 1996).

2.2. DATA COLLECTION

2.2.1. Landscape-Water Chemistry Data

2.2.1.1. Landscape data

Land use/land cover (LULC), soil, geology, hydrography, and elevation databases were used to describe landscape features within the study watershed. Stream networks were digitized from 30 m National Elevation Data (NED) using ArcGIS (ArcView 9.2, 2007) and ArcHydro (Maidment, 2002) software. The USGS National Hydrography Dataset (NHD) was used to verify the stream delineation determined by the ArcHydro flow-direction/accumulation grids. The catchment area of the Pedernales watershed and the sub-catchments above sampling points were delineated using catchment-processing tools in ArcHydro software (Dodds and Oakes, 2006). Landscape data were collected from state and nationwide databases (Table 1), and quantified at three spatial scales (1) entire sub-catchment above sampling location, (2) sub-catchment 200 m riparian buffer, and a (3) 2 km stream reach riparian buffer (Morley and Karr, 2002). The riparian and stream reach width of 200 m was chosen based on previous studies that evaluated riparian function (Osborne and Wiley, 1988; Gregory et al., 1991; Morley and Karr, 2002), and to

compliment the resolution of the available dataset. Land cover attributes were analyzed as percentages at each spatial scale.

Land cover data were classified from the Multi-resolution Land Characteristics Consortium (MRLC) National Land Cover data set (NLCD 2001) (Homer et al., 2007). These data were derived from Landsat Thematic Mapper (TM) data at a 30 m resolution containing 21 classes that reflect LULC conditions in 2001 (Vogelmann, 2001). Large LULC changes have not occurred in the study area since 2001 (Oliver, 2008). Many described land cover classes did not occur or accounted for less than 1% of the study area, and were therefore excluded from analyses (Dodds and Oakes, 2008). The remaining classifications were grouped into five categories (cropland, grassland, forest, scrub, and urban) based on the level I classification scheme developed by Anderson et al. (1976) created for natural resource applications. Open water was not included as a land cover classification (Johnson et al., 1997; Dodds and Oakes, 2008).

Soil type was classified using National Resource Conservation Service, Soil Survey Geographic data set (NRCS; SSURGO, 2004) at the 1:24,000 scale. Soil series data were further aggregated using the NRCS Hydrologic Soil Group (HSG) value of each soil series. The HSG was determined by the NRCS based on measured rainfall, runoff, and infiltration data (USDA NRCS, 2007). Each soil series was given an A through D value based on soil composition, runoff potential, and soil permeability. For example, NRCS described HSG value A as 90% sand, 10% clay, thus having low runoff potential and high permeability. With each descending HSG value, the percentage of sand decreased and the percentage of clay increased. The aggregation of the soil series data allowed for comparison of soil characteristics with surface water chemistry.

Geologic attributes were classified from the University of Texas, Bureau of Economic Geology, Geologic Atlas of Texas (GAT) map sheets digitized at the 1:250,000 scale. These data include the geologic time period and formation description of the rock units in the study area. Rock units were evaluated for composition, and grouped based on major rock type. The three dominant geologic periods were Quaternary (sandstone/shale), Cretaceous – Cambrian (limestone/dolomite), and Precambrian (granitic/metamorphic). Once rock groups were created (i.e., sandstone/shale, limestone/dolomite, granitic/metamorphic) it was determined that the geology of the study area was relatively homogenous. Due to the coarser resolution of the available geologic data and the homogenous nature of the rock types, only catchment scale geologic attributes were quantified. Topographic variability was quantified at each spatial scale using standard deviation of slope (hereafter, slope) (Sliva and Williams, 2001).

Features common to all spatial scales were also included in analyses. The distance of the sampling location from the mouth of river was determined to describe geographic position in the landscape (river km). To characterize relative spring influence, distance of the sampling locations from nearest spring outfall was measured using the flow-path tracing tool in ArcHydro software. Spring location data were obtained from the NHD available at the 1:100,000 scale. Although this did not quantify spring size/discharge amount, or number of springs near the sample location, it did offer a measure of relative spring proximity.

United States Geological Survey (USGS) and Lower Colorado River Authority (LCRA) stream discharge data were acquired to characterize watershed discharge

conditions. Stream discharge data included four mainstem Pedernales and two perennial tributary gauging stations that record stream stage and discharge in 15-minute intervals (Figure 1). Although the absolute value is only correct at the location of the specific station, the numbers offer a quantitative way to monitor flows on the sample date and antecedent conditions. Sample-associated values were determined using the instantaneous discharge value from the gauging station nearest to the sampling location at the time increment closest to the sample date and time.

2.2.1.2. Sampling and water chemistry data

To characterize surface water chemistry, 13 sampling stations were selected within the Pedernales River watershed. Sub-catchments were delineated above each sample location, and ranged in size from 77 to 2,913 km². After sampling was initiated, it was determined that two sampling stations were within 10 km of wastewater effluent (Appendix A.1), and illustrated soluble reactive phosphorus concentrations ranging from 2 to 1200 µg/L (Appendix A.2). These sampling stations were excluded from analyses since point source pollution influences will likely mask landscape effects (Dodds and Oakes, 2006 and 2008). Therefore, analyses were conducted on 11 (six Pedernales mainstem and five tributary) sampling stations (Figure 1).

Water chemistry data were collected monthly from July 2007 to August 2008. Sampling was conducted throughout the year to capture the seasonal and hydrological variation characteristics of the study area. Seasonal delineations were based on the distribution of the temperature curve and discharge patterns for the study period (Figure 2) (Sliva and Williams, 2001), and were determined as the following: fall (October – November), winter (December – February), spring (March – May), and summer (June –

September). Each site was sampled for water temperature, pH, dissolved oxygen (DO), and specific conductivity (COND) using a HydrolabTM Minisonde with readings taken from well-mixed areas having visible stream flow. Discrete samples were also collected at each site location in acid-washed high-density polyethylene bottles, stored on ice, transported to the laboratory, and stored at either 1.7 or -15 °C until analysis could be conducted. Replicate samples were taken at three sampling stations and averaged as concentrations generally fell within 15% of original sample. Water chemistry variables included: total phosphorus (TP), soluble reactive phosphorus (SRP), nitrate (NO₃-N), dissolved organic carbon (DOC), acid neutralizing capacity (ANC), turbidity (TURB), and chlorophyll *a* (chl *a*).

Soluble reactive phosphorus and NO₃-N samples were filtered through nominal pore size 0.7 µm Whatman GF/F glass fiber filters. Nitrate was determined using second-derivative UV spectroscopy (Crompton et al., 1992), and SRP was determined using the ascorbic acid method (Murphy and Riley, 1962). Total P samples were digested by potassium persulfate-autoclave method (Strickland and Parsons, 1972), and analyzed as SRP. Dissolved organic carbon was measured on a Shimadzu TOC-V_{CSH} Analyzer on duplicate filtered (through ashed GF/F) water samples. Acid neutralizing capacity was measured by Gran titration to pH 4.8 using 0.02 N H₂SO₄ (Wetzel and Likens, 1991). Chlorophyll *a* was determined in DMSO-acetone extracts (Burnison, 1980) with fluorometric analysis, and turbidity via a Fisher Scientific Turbidimeter.

2.2.2. Long-term Data

To evaluate seasonal and long-term temporal trends in nutrient chemistry, an additional dataset was incorporated into analysis. These data were collected by the LCRA in addition to the discharge data described in the previous section. The LCRA conducted monthly/bi-monthly sampling and analysis of $\text{NO}_2\text{-N} + \text{NO}_3\text{-N}$ (hereafter, $\text{NO}_3\text{-N}$), ammonia ($\text{NH}_3\text{-N}$), organic N (ON) (calculated as Kheldal minus $\text{NH}_3\text{-N}$), SRP, TP, and total organic carbon (TOC) at the four mainstem stations for up to a twenty-four year period (length of database varied by station, 1984-2008) (Figure 1). Any concentration recorded as below detection limit was assumed half of the detection limit value.

In-stream nutrient concentrations are strongly linked to flow regime; therefore, the data was first classified by discharge conditions (Dodds and Oakes, 2008). Discharge periods were created using the mean daily discharge measurements for the data period (1984-2008) from the two USGS gauging stations located in the central region of the study area (P80 and P150). Quartiles were examined and discharge data was classified into two groups, 10% to the median (low-discharge conditions), and from the median to the 90% (high-discharge conditions). Each water chemistry observation was then classified by the instantaneous discharge value associated with that sample. To avoid drought concentrations (< 10%) or storm pulse events (> 90%), samples taken during either condition were excluded from analyses. The two discharge groups (i.e., low and high discharge conditions) were then evaluated for seasonal and long-term temporal trends.

2.3. STATISTICAL ANALYSIS

2.3.1. *Landscape-Water Chemistry Data*

Water chemistry and landscape data were analyzed using descriptive and multivariate analysis. Prior to conducting analyses, distribution curves were evaluated for all variables and appropriate transformations were applied to those exhibiting a non-normal distribution. Water chemistry parameters were typically $\log_{10}(x+1)$ transformed, while proportions (landscape features) were generally arcsin-square root transformed.

Principal Components Analysis (PCA) was initially explored used to evaluate the distribution of water chemistry variables across site and season (Stewart et al., 2001). Initial PCA identified that water chemistry factors with the largest loading were those subject to diel patterns (temp, DO, pH) (Appendix B). To focus on the variation of the other chemical constituents, variables exhibiting diel patterns were excluded from further PCA and Redundancy Analysis (RDA). The preliminary PCA also illustrated that summer and winter observations differentially ordinated along PC axis I, while fall and spring samples generally overlaid the subsequent seasons. The data was therefore grouped in a fall-winter and spring-summer manner (hereafter, winter and summer respectively) for RDA. PCA axis I also identified some separation across mainstem and tributary sampling stations. These procedures identified groups that collapsed the dataset for descriptive analysis (means and coefficients of variation [CV %]) by summer versus winter season, and mainstem versus tributary sampling stations.

Landscape variables quantified using GIS technologies were used to describe the physical attributes of the Pedernales River watershed. Landscape variables are often highly correlated and do not adhere to assumptions of independence. For example, an

increase in one LULC characteristic implies a decrease in the other (i.e., increase % cropland, thereby decrease % forest or scrubland). Additionally, the smaller spatial scales (i.e., riparian and stream reach) are a subset of the catchment scale, thus differential relationships will be affected by how closely the riparian/stream reach LULC mirrors that of the catchment LULC (Allan, 2004). In order to reduce the effects of autocorrelation and multicollinearity, a Spearman rank correlation matrix was determined using SPSS. The Spearman's matrix was used to exclude any variable that was highly correlated ($r > 0.70$) within and across spatial scales and landscape features. For example, the results of the Spearman's matrix identified that crop and urban land use in the catchment and riparian corridor were highly correlated ($r = 0.93$ and 0.88 , $P < 0.0001$), thus effects could not be independently evaluated. However, there was not a strong correlation between catchment cropland and stream reach cropland, therefore land use-water chemistry relationships across these spatial scales could be examined. This data reduction technique created a full model (Table 2) of relatively independent landscape variables.

The full model of landscape features was related to water chemistry measures using RDA (CANOCO 4.5; ter Braak, 1988 and 2002). This technique identified which landscape factors had the largest influence on chemical ordination, and quantified the variation explained by these factors (Sliva and Williams, 2001). Redundancy Analysis was conducted independently across the summer and winter season, and results were tested for significance ($P \leq 0.05$) by a Monte Carlo permutation test using 9,999 iterations.

2.3.2. Long-term Data

The long-term dataset was used to characterize seasonality in nutrient chemistry under contrasting discharge conditions. Incorporating the long-term dataset also allowed for direct comparison of the 2007-2008 collected data. Prior to conducting seasonal analysis, I first had to determine if the four mainstem stations differed in global nutrient chemistry (TOC, ON, NO₃-N, NH₃-N, TP, and SRP). As expected, the stations did differ across the low (MANOVA, Wilks' Lambda = 0.388, $P < 0.0001$) and high (Wilks' Lambda = 0.514, $P < 0.0001$) discharge periods; however, post-hoc analysis confirmed that the two stations in closest proximity (P103 and P80) were consistently similar. Therefore, the data from these two sites were pooled to evaluate seasonal and long-term temporal trends. Seasonal differences were determined using a one-way Analysis of Variance (ANOVA) with season as the independent factor, and supplemental post-hoc Tukey's multiple comparison tests were conducted with a $P \leq 0.05$ significance.

Long-term trend analysis was conducted to determine if nutrient chemistry has changed from 1984-2008. The data was independently evaluated across discharge periods to project how increased or decreased stream flows might influence nutrient concentrations over time. To determine if nutrient chemistry has changed, deviation from a long-term mean was analyzed using simple linear regression. Mean nutrient concentrations from 1984 - 2008 were calculated for each discharge period, and samples within each period were averaged by year. The slope of the relationship was calculated to determine if it was significantly different from zero, thus indicating a long-term increasing or decreasing trend. Nutrients illustrating a significant long-term trend were then analyzed using a generalized least squares (GLS) model to determine if identified

trends were still significant while accounting for yearly hydrologic variation and temporal autocorrelation. A lag interval of one year was chosen due to missing years in the long-term dataset. A likelihood ratio test (LRT) was used to determine which model better explained long-term nutrient variation. All ANOVA, post hoc, GLS, and LRT analyses were conducted using the statistical package R 2.8.1.

3. RESULTS

3.1. LANDSCAPE-WATER CHEMISTRY DATA

3.1.1. *Landscape Attributes*

Landscape features, including land use, soil composition, and geology, were relatively homogenous in all sub-catchments of the Pedernales watershed (Figure 3). Scrubland/savannah was the dominant land cover class (sub-catchment mean and range: 58.70%, 53 - 71%); however, these areas are often used as livestock rangelands (Oliver, 2008) and should not be considered completely undisturbed. The percentages of more highly disturbed land use (urban, crop, and grassland agriculture) accounted for less than 50% of land cover at all spatial scales, ranging between 6 - 19 %, 11 - 40%, and 3 - 40% (sub-catchments, riparian corridor, 2 km stream reach, respectively). The Pedernales watershed contains mostly clay soils (sub-catchment HSG D mean and range: 61.57%, 24 - 85%); however, near-stream areas did illustrate higher proportions of coarse-textured sands or gravel, and limestone bedrock material (riparian corridor and 2 km stream reach HSG A and B combined: 4 - 70%, and 0 - 82%, respectively). Geology was similar across all sites, except for G4, G29, and downstream mainstem Pedernales stations,

which contained Precambrian granitic rock (sub-catchment mean and range: 1.29%, 0 - 8%) unlike the sedimentary limestone/dolomite located throughout the majority of the study area (sub-catchment Cretaceous - Cambrian rock mean and range: 94.22%, 89 - 99%).

Mainstem sampling stations spanned a total of 143 river kilometers, and headwater and tributary sampling stations were typically closer to spring outfall locations (spring outfall mean and range: 19.96 km, 1 - 47 km). Topography was comparable across all spatial scales, except at P45 and P24 where standard deviation of slopes adjacent to the sampling locations were greater (2 km stream reach: 15 and 16%, respectively) than the sub-catchments (mean and range: 4.80%, 2 - 10%) or riparian corridors (mean and range: 5.30%, 2 - 8%).

3.1.2. *Water Chemistry*

Water chemistry data were collected throughout the year in water temperatures ranging from 7.25 to 36.15°C across a wide range of discharge conditions (P80 mean daily discharge range: 0.09 - 1,124 m³/s, Figure 2). Total P, SRP, DOC, TURB, and pH were highest at mainstem stations during the summer (mean \pm 1 SD: 14.0 \pm 13.2 μ g/L, 5.4 \pm 6.5 μ g/L, 2.4 \pm 0.8 mg/L, 9.9 \pm 10.8 NTU, 8.3 \pm 0.3, respectively), whereas NO₃-N (1109.8 \pm 325.4 μ g/L) and COND (640.5 \pm 42.8 μ S/cm) were highest during the winter (Table 3). Tributaries illustrated the highest ANC (5.4 \pm 1.0 meq/L) and chl *a* (3.4 \pm 6.7 μ g/L) concentrations in the watershed during the summer season.

Principal Components Analysis produced three gradients that explained 62% of the variation in collected water chemistry measures (Figure 4). Principal axis I explained

30% of the total variation and appeared to describe a nutrient-loading gradient (Figure 4a). Samples with the largest positive loadings on PCA axis I had high TP (0.88), TURB (0.75), and SRP (0.61), and lower negative loadings of COND (-0.54) concentrations. The second PCA axis explained 18% of the total variation and incorporated ionic species, including COND (0.72) and ANC (0.48). Sample stations also illustrated some separation along PCA axis I and II with mainstem Pedernales stations having larger loadings of TURB, TP, and SRP along axis I, whereas tributary stations illustrated larger loadings of COND, DOC, and ANC along axis II. Principal axis III explained 13% of the total variation and appeared to reflect a particulate gradient. Samples with larger loadings along PCA axis III were summer samples with high loadings of chl *a* (0.66), ANC (0.45), and TURB (0.26), and lower negative loadings of dissolved compounds (SRP (-0.53) and DOC (-0.22)) (Figure 4b).

3.1.3. *Landscape-Water Chemistry Relationships*

Landscape features explained 52% of the variability in winter water chemistry (Figure 5). Factors explaining the largest variation along RDA axis I were slope (biplot score = 0.83), sub-catchment urban (0.58), and riparian grassland land use (0.43). Factors with strong positive loadings on RDA axis II were stream discharge (0.71) and stream reach cropland (0.51), whereas riparian forests (-0.82) and clay-dominated soils (-0.50) illustrated large negative loadings. Additional landscape features explained variation along RDA axis II with weaker loadings from sub-catchment sandy soils, crop, and grassland agriculture (0.40, 0.39, -0.40, respectively), headwater reaches (0.35), and spring outfall (0.31) (Table 4). Turbidity was positively associated with RDA axis I,

thereby urban land use and steep slopes, best described by tributary station M22 (Figure 5a). Specific conductivity and ANC were highly correlated and negatively associated with RDA axis I, particularly at tributary station G29. Chemical parameters positively associated with RDA axis II were $\text{NO}_3\text{-N}$ and DOC, therefore greater stream discharge and local crop, specifically more abundant at stations closer to headwater springs (P163, P153, and P167). Nitrate and DOC were negatively associated with higher percentages of riparian forests with clay-dominated soils, which best characterized tributary stations C18, G4, and L10.

Landscape features accounted for slightly less variation in summer water chemistry (48%) (Figure 5b). Consistent with the winter season, slope (-0.37) had strong loadings on RDA axis I; however, stream discharge (-0.71) illustrated the largest loadings and urban areas shifted to RDA axis II. Sub-catchment land use illustrated a stronger influence on summer water chemistry with large positive loading from urban (0.70), grassland (0.54), and crop (0.50) agriculture along RDA axis II, whereas headwater reaches had large negative loadings (-0.63). Stream reach features had weaker negative loadings along RDA axis II, including crop (-0.38), grassland (-0.35), and clay soils (-0.35). Similar associations were also found along RDA axis I with respect to COND, ANC, and TURB. However, during the summer $\text{NO}_3\text{-N}$ was negatively associated with RDA axis I, therefore typically higher during increased stream discharge and in sub-catchments with steeper slopes. Redundancy axis II illustrated an urban and agricultural land use gradient associated with increased concentrations of DOC, chl *a*, TURB, and TP, particularly at sampling stations M22 and P63.

Landscape features accounted for slightly more variation in winter (52%) versus summer (48%) water chemistry. Winter water chemistry reflected riparian and stream reach landscape features, whereas summer water chemistry was more strongly associated with sub-catchment features. Larger differences between summer and winter landscape-water chemistry associations were observed with individual chemical variables. Nitrate, COND, and ANC were better explained in the winter, whereas TP, DOC, and chl *a* were better explained by landscape attributes in the summer (Table 4). However, there were some contradictory associations found across season and spatial scales. In the summer NO₃-N was positively associated with sub-catchment sandy soils, whereas negative associations were found in the winter. Also, in the summer season opposing relationships were found across spatial scales in that TP, chl *a*, and DOC were positively associated with sub-catchment agricultural land use and negatively associated with stream reach agriculture.

3.2. LONG-TERM DATA

3.2.1. *Seasonal Patterns*

Nutrient chemistry seasonality was generally consistent across discharge periods with a few notable exceptions (Figure 6). Nutrient concentrations were highest in the spring and summer for all species except for NO₃-N and SRP, which illustrated higher winter concentrations, particularly during the low discharge period (seasonal means \pm 1 SD: 750 \pm 79 and 20 \pm 7 μ g/L) (Figure 6a). The largest difference across discharge period was found in NO₃-N concentrations in the fall, with higher concentrations in high flows (183 \pm 95 and 680 \pm 119 μ g/L, low and high discharge respectively) (Figure 6a,b).

The other N-related species (ON and $\text{NH}_3\text{-N}$) exhibited seasonally lower winter concentrations, particularly in ON during low flows ($257 \pm 35 \mu\text{g/L}$) and $\text{NH}_3\text{-N}$ during high flow conditions ($20 \pm 6 \mu\text{g/L}$). Nitrate also differed across discharge periods in that low flow spring and summer concentrations were approximately double (58 ± 9 and $57 \pm 24 \mu\text{g/L}$, respectively) high flow concentrations (30 ± 15 and $40 \pm 12 \mu\text{g/L}$, respectively). Surface water TOC was consistently low (seasonal mean range: 2.6 - 4.0 mg/L) with correspondingly low planktonic algae productivity (chl *a* seasonal range: 1.7 - 4.6 $\mu\text{g/L}$). Phosphorus-related parameters illustrated the highest within season variation (CV range SRP and TP: 15 - 160%).

The long-term seasonality was comparable to the data collected in 2007 and 2008, with higher summer concentrations in all species except $\text{NO}_3\text{-N}$. Large differences in water chemistry across the 2007 and 2008 summer sampling mirrored the conditions of the discharge groups of the long-term dataset. During the summer of 2007, there were several storm pulses orders of magnitude higher ($6.4 - 1,124 \text{ m}^3/\text{s}$, P80 mean daily discharge range) than average discharge conditions ($5 \text{ m}^3/\text{s}$; P80, 1940-2008). However, the summer of 2008 was characterized by drought conditions ($0.09 - 1.56 \text{ m}^3/\text{s}$), and correspondingly lower surface water nutrient concentrations. This was consistent with the patterns found in the long-term dataset, particularly evident in $\text{NO}_3\text{-N}$ concentrations. Nitrate averages differed by an order of magnitude across the summer 2007 ($400 \pm 183 \mu\text{g/L}$) and 2008 ($54 \pm 72 \mu\text{g/L}$) at the P103 and P63 stations (i.e., stations in closest proximity to long-term stations).

3 2.2. Long-term Trends

Nitrate, ON, and SRP illustrated significant trends from 1984 to 2008. Nitrate concentrations have increased across the low and high discharge period (GLS: $\beta_1 = 1.06$, $t_{18} = 2.35$, $P = 0.03$; $\beta_1 = 1.04$, $t_{16} = 2.56$, $P = 0.021$). Soluble reactive P has increased ($\beta_1 = 1.05$, $t_{18} = 2.80$, $P = 0.012$), and ON has decreased ($\beta_1 = -1.02$, $t_{18} = -2.24$, $P = 0.037$) during the low discharge period (Figure 7).

To determine if significant trends were correlated with climatic conditions (precipitation) rather than landscape features, stream discharge was incorporated into linear models. It was determined that only $\text{NO}_3\text{-N}$ was correlated with stream discharge under high flow conditions ($\beta_1 = 3.02$, $P = 0.004$) (Figure 8), though the increasing temporal trend was still significant after incorporating discharge into the GLS models ($\beta_1 = 1.03$, $t_{15} = 2.55$, $P = 0.022$). A temporal autocorrelation term was also evaluated to determine if trends were the result of stream concentrations from previous years. As expected, a temporal autocorrelation term did not explain significant additional variation in the relationship between $\text{NO}_3\text{-N}$, SRP, or ON and sample year ($X_1^2 = 0.024$, $P = 0.44$; $X_1^2 = 0.046$, $P = 0.42$; and $X_1^2 = 0.155$, $P = 0.35$) during low flow conditions, or $\text{NO}_3\text{-N}$ ($X_1^2 = 1.05$, $P = 0.15$) under high flows. The absence of temporal autocorrelation indicates that there was a not significant residual effect of chemical concentrations from previous years.

4. DISCUSSION

4.1. LANDSCAPE-WATER CHEMISTRY DATA

The present study found that agricultural and urban land use along with geologic and topographic features influence adjacent surface water chemistry in a subtropical karstic river system. The strongest land cover associations were found with directly adjacent (riparian corridor and 2 km stream reach) landscape features and dissolved species ($\text{NO}_3\text{-N}$, DOC), whereas sub-catchment land use, geology, and soil composition were associated with conservative ions and particulates (COND, ANC, TP, TURB, chl α). However, standard deviation of slope and stream discharge illustrated some of the largest correlations with winter ($\text{NO}_3\text{-N}$, TURB, DOC) and summer ($\text{NO}_3\text{-N}$, TP, TURB) water chemistry. The prevalence of topography and discharge as primary predictors, along with relationships found between $\text{NO}_3\text{-N}$, TP and natural watershed features (i.e., soil composition and geologic formation), indicates that multiple transport mechanisms are influencing the chemical composition of surface waters in the Pedernales River watershed.

This study supports previous investigations that report degraded water quality in crop, rangeland, and urban landscapes (Biggs, 1995; Townsend et al., 1997; Carpenter et al., 1998). The influence of crop agriculture on stream water $\text{NO}_3\text{-N}$ has been consistently documented (Osborne and Wiley, 1988; Lenat and Crawford, 1994; Johnson et al., 1997; Dodds and Oakes, 2006 and 2008), as well as the influence of agricultural and urban land use on TP, SRP, DOC, TURB, and chl α (Biggs, 1995; Hunsaker and Levine, 1995; Soranno et al., 1996).

In addition to nutrient loading, urban land use is known to increase the conservative ionic composition of surface waters (Lenat and Crawford, 1994; Paul and Meyer, 2001); however, we found that ANC and COND were consistently negatively associated with urban areas. The study area has low percentages of urban land use at all spatial scales (0 – 3%) and is characterized by carbonate-sedimentary geology, thus the ionic chemistry is likely controlled by geologic over anthropogenic landscape features (Johnson et al., 1997). Additionally, the Pedernales watershed appears to have a unique ionic chemistry compared to other streams within the Edwards Plateau. Groeger and Gustafson (1994) characterized the ionic chemistry of seven major streams located throughout the ecoregion and documented COND ranging from 394 to 535 $\mu\text{S}/\text{cm}$, whereas the Pedernales ranged from 335 – 990 $\mu\text{S}/\text{cm}$. From these data, there appears to be an increasing evaporite influence on COND associated with the northeast region of the Edwards Plateau.

Riparian corridor and stream reach landscape features explained a larger portion of the variation in $\text{NO}_3\text{-N}$ and DOC, whereas sub-catchment features were more strongly associated with in-stream particulates. The ability of riparian corridors to mediate $\text{NO}_3\text{-N}$ export through vegetative uptake and denitrification has been consistently documented (Osborne and Wiley, 1998; Sliva and Williams, 2001; Dodds and Oakes, 2006 and 2008), particularly in anaerobic clay-dominated substrates (Lamontagne et al., 2005; Chen et al., 2009) such as those found in the riparian corridors of the Pedernales River. Redundancy Analysis illustrated that the strongest predictors of DOC illustrated a seasonal shift from riparian forests in the winter to sub-catchment urban and agricultural land use in the summer. This is likely due to a shift from allochthonous leaf litter-produced C in the

winter (Arango and Tank, 2008) to autochthonous biologically produced C in the summer (Quinn et al., 1997; Herrman et al., 2008). Spring and summer surface water DOC has been directly linked to runoff from agricultural areas (Quinn et al., 1997; Arango and Tank, 2008), and also indirectly through increased biological activity associated with nutrient loading (Townsend and Riley, 1999; Biggs, 2000; Dodds et al., 2002b). This is supported by the strong correlation found between DOC, TP, and chl *a* in the summer PCA and RDA.

Total P was correlated with urban and agricultural land use at the largest spatial scale, though little total variation was explained across either season. The association with larger spatial scales and lack of predictability has been attributed to sorption processes and the tight linkage of P with individual precipitation events (Johnson et al., 1997; Townsend and Riley, 1999; Jones et al., 2001; Sliva and Williams, 2001). This was also influenced by the study design, since riparian crop and urban land use were removed from analysis. Even though stream reach features were included, it is difficult to accurately exclude the riparian corridor as a primary predictor.

Stream discharge and slope were primary predictors of summer and winter water chemistry, indicating the overriding influence of hydrology in these streams. Since the study area is characterized by increased precipitation during the spring and summer, a higher degree of hydrologic connectivity would explain the stronger connection to sub-catchment landscape features during this time (Johnson et al., 1997; Dent and Grimm, 1999; Sorranho et al., 2006). Hydrologic transport mechanisms could also explain some of the contradictory associations found across spatial scales. Total P, DOC, and chl *a* illustrated a positive sub-catchment and negative stream reach association with

agricultural land use. The additional associations with stream discharge, slope, and clay-dominated soils indicate that sorption and downstream transport could be occurring, leading to dissociation with localized land use (Johnson et al., 1997; Sliva and Williams, 2001).

Nitrate also illustrated contradictory associations across season and spatial scale. Nitrate was positively associated with local crop agriculture, while negatively associated with sub-catchment crop. Crop agriculture at the sub-catchment scale was correlated with highly permeable sandy soils, and these areas have a higher potential to transport $\text{NO}_3\text{-N}$ to groundwater via leaching (Lamontagne et al., 2005; Sabater et al., 2003). Divergent transport is supported by the strong influence of the riparian corridor in the winter, but diminished association in the summer. Riparian vegetation may not effectively mediate $\text{NO}_3\text{-N}$ concentrations under extreme hydrological conditions. Nitrate entering surface waters from groundwater contribution during low flow conditions can enter below the root zone (Hill, 1996; Arango and Tank, 2008), whereas high flow conditions can create a flushing effect where transport occurs too quickly for terrestrial processing (Morecroft et al., 2000; Butturini et al., 2003). This could also be amplified by conduit groundwater recharge of the study area, which potentially limits terrestrial nutrient processing (Hill, 1996; Houser et al., 2005).

4.2. LONG-TERM DATA

Temporal trends were apparent with distinct seasonality in most nutrient species. Seasonal trends were consistent with the data collected throughout the watershed during 2007 and 2008, particularly in relation to the differences found across discharge periods.

Long-term trends were also found in $\text{NO}_3\text{-N}$, ON , and SRP , and appear to be related to land cover change.

Soluble reactive P and TP illustrated with highest within season variability, similar to data collected in 2007-2008. There was a distinct peak in SRP in the winter of the low-discharge period (Figure 6a), likely associated with the City of Fredericksburg Wastewater Treatment Plant located approximately 36 and 59 km upstream of sample stations P103 and P80. Biological activity is likely not great enough to assimilate the added dissolved phosphorus during the winter months (Carpenter et al., 1988; Biggs, 2000).

Nitrate exhibited the largest seasonal variation, which is generally contributed to differences in biological activity (Arango et al., 2008), water residence time (Dent and Grimm, 1999; Herrman et al., 2008), and groundwater recharge rates (Scanlon et al., 2006; Kingsbury, 2008). Nitrate was consistently highest during the winter, likely associated with high groundwater contributions flowing beneath agricultural areas (Kemp and Dodds, 2001; Chen et al., 2005). The largest variation across discharge groups was found in fall $\text{NO}_3\text{-N}$ concentrations. Considering the long subtropical growing season of the study area (i.e., 237 - 300 days) (NCDC, 2002) and longer water residence time associated with the low flow period, conditions are optimal for benthic productivity (Biggs 1995 and 2000). This can increase overall in-stream N demand, thus reducing $\text{NO}_3\text{-N}$ concentrations (Dent and Grimm, 1999; Arango and Tank, 2008). This is supported by the 10-fold difference in $\text{NO}_3\text{-N}$ concentration across the summers of 2007 and 2008 (characterized by high and low flow regimes, respectively).

Long-term trends in $\text{NO}_3\text{-N}$, ON , and SRP appear to be related to land cover change. The high winter SRP concentrations were coupled with long-term increases of SRP found only during the low-discharge period. The increasing trend in SRP is likely due to increased population density of the study area (USCB, 2000). Long-term trends in $\text{NO}_3\text{-N}$ were related to annual average atmospheric $\text{NO}_3\text{-N}$ deposition (precipitation weighted concentration) collected from the National Atmospheric Deposition Program (NADP) monitoring station nearest to the study area (Sonora, TX). Atmospheric $\text{NO}_3\text{-N}$ deposition has not increased over the long-term data period ($t_{17} = 0.299$, $P = 0.768$), and the inter-annual variability was not related to stream $\text{NO}_3\text{-N}$ variability during low-discharge ($t_{17} = -0.344$, $P = 0.735$) or high-discharge period ($t_{16} = -0.865$, $P = 0.400$) (Figure 8b). However, the average atmospheric $\text{NO}_3\text{-N}$ concentration for the data period was approximately 1000 $\mu\text{g/L}$, which is consistent with the surface water concentrations of the study area. The findings that atmospheric $\text{NO}_3\text{-N}$ deposition did not increase over the data long-term data period suggests that long-term increases in $\text{NO}_3\text{-N}$ are associated with land cover change (Vitousek et al., 1997; Chen et al., 2005).

4.3. CONCLUSIONS

Subtropical streams differ from temperate streams largely in the length of the growing season and higher overall ambient air temperature (Chen et al., 2005; Dodds, 2002a), but can also potentially differ in percent canopy cover (Dodds, 1997; Mosisch et al., 2001). This combination of factors can lead to increased autotrophic activity (Mosisch et al., 2001; Chen et al., 2005), particularly with the added effects of inorganic nutrient loading (Biggs, 1995 and 2000; Udy et al., 2006). Increased autotrophic biomass

was visually prevalent in areas lacking a forested riparian corridor within the Pedernales watershed; however, this was only true after an extended period of low flow conditions.

Land cover conversion and nutrient addition can lead to shifts in species assemblages and benthic productivity, thus altering overall ecosystem health (Vitousek et al., 1997; Houser et al., 2005; Udy et al., 2006). The overall influence of converted land use on stream water chemistry in the Pedernales watershed was consistent with previous research, despite differences in climatic conditions. The surface water chemistry of the study area appears to be more strongly influenced by the stochastic nature of the precipitation regime, as the large seasonal and inter-annual variability will regulate flow path and terrestrial processing of dissolved and particulate materials and in-stream biological activity. Changes in hydrological connectivity will ultimately shift the scale landscape influences surface water chemistry, and the relative influence of headwater tributaries.

Table 1. State and nationwide databases used to quantify landscape features.

Database	Scale	Source
Hydrography	1:100,000	USGS NHD
Soils	1:24,000	NRCS SSURGO
Topography	1:24,000	USGS NED
LULC	1:100,000	NLCD 2001 (MRLC)
Geology	1:250,000	GAT

Table 2. Quantified landscape variables. **X** denotes variables included in RDA.
See Methods

Landscape feature	Full Model			
	<i>Common</i>	<i>Catchment</i>	<i>Riparian</i>	<i>Reach</i>
<i>LULC (%)</i>				
Grassland		X	X	X
Forest		X	X	X
Cropland		X		X
Scrub				
Urban		X		X
<i>Soils (%)</i>				
A		X		
B				
C			X	X
D				
<i>Geology (%)</i>				
Quaternary Rock		X		
Cretaceous - Cambrian Rock				
Precambrian Rock		X		
<i>Geographic/Topographic</i>				
Mean slope (%)				
St Dev. slope	X			
Distance from spring outfall (km)	X			
River kilometer (km)	X			
Instantaneous Discharge (m ³ /s)	X			

Table 3. Seasonal means, coefficients of variation [CV(%)], minima and maxima for selected water chemistry variables. n_1 = number of sample sites at Pedernales mainstem and tributary sub-catchments; n_2 = number of samples in each season.

	Mainstem ($n_1=6$)						Tributary ($n_1=5$)					
	Fall-Winter ($n_2=30$)			Spring-Summer ($n_2=54$)			Fall-Winter ($n_2=25$)			Spring-Summer ($n_2=43$)		
	Mean [CV%]	Min	Max	Mean [CV%]	Min	Max	Mean [CV%]	Min	Max	Mean [CV%]	Min	Max
NO ₃ -N (µg/L)	1110 [29]	491	1686	323 [78]	10	917	241 [90]	10	716	156 [100]	10	567
TP (µg/L)	5.3 [89]	0.2	17.1	14.0 [95]	3.4	70.4	4.4 [99]	0.2	19.1	8.7 [89]	0.2	29.0
SRP (µg/L)	1.4 [147]	0.1	10.5	5.4 [120]	0.1	33.0	1.8 [119]	0.1	8.5	4.3 [133]	0.1	26.5
DOC (mg/L)	2.05 [28]	0.82	3.34	2.41 [33]	0.44	4.84	1.46 [53]	0.44	3.50	2.02 [55]	0.44	5.89
Chl a (µg/L)	1.52 [68]	0.23	3.75	1.81 [86]	0.36	7.50	2.14 [92]	0.27	6.78	3.43 [196]	0.16	27.75
Sp. Cond (µS/cm)	641 [7]	550	745	605 [20]	335	818	628 [18]	473	873	613 [23]	406	990
Turbidity (NTU)	3.8 [31]	2.2	8.6	9.9 [110]	2.6	40.0	4.2 [97]	2.0	22.0	4.2 [80]	2.4	24.0
Alkalinity (meq/L)	4.82 [8]	4.08	5.60	4.59 [16]	3.88	9.24	5.34 [14]	4.04	6.88	5.37 [19]	3.64	8.25
Temp (°C)	15.65 [31]	7.25	24.40	27.67 [13]	19.42	34.03	15.54 [28]	8.23	23.51	26.71 [17]	18.64	36.15
Dissolved O ₂ (mg/L)	9.47 [9]	7.66	10.78	7.74 [11]	5.27	9.99	9.25 [11]	6.68	11.29	8.02 [24]	6.03	16.34
pH	8.20 [3]	7.60	8.48	8.31 [3]	7.07	8.79	8.21 [2.2]	7.90	8.70	8.12 [3]	7.40	8.56

Table 4. (a) Landscape features illustrating the strongest influence on ordination of winter and summer water chemistry. *P* values derived from Monte Carlo permutation tests. Factor scores illustrated if greater than ± 0.30 . (b) Biplot scores of water chemistry variables with percentage of total variance explained by indicated landscape features.

<i>a</i>	Winter			Summer		
	(52%, <i>P</i> = 0.0001)			(48%, <i>P</i> = 0.0001)		
	Axis I	Axis II	% <i>Exp</i>	Axis I	Axis II	% <i>Exp</i>
Q		0.71		-0.71		
KM		0.35			-0.63	
SPR		0.31				
SD SLP	0.83			-0.37	0.55	
Geo Q				0.31	0.45	
Geo pC				0.34		
Cat Soil A		0.40			0.54	
Cat FOR						
Cat GRS		-0.40		0.35	0.54	
Cat CRP		0.39			0.50	
Cat URB	0.58				0.70	
Rip FOR		-0.82		0.31		
Rip GRS	0.43					
Rip Soil C		-0.50		0.39		
2K GRS					-0.35	
2K CRP		0.51			-0.38	
2K Soil C					-0.35	
<i>b</i>						
NO ₃ -N	-0.04	0.93	92	-0.53	-0.45	72
TP	0.09	0.11	19	-0.15	0.30	24
SRP	-0.09	-0.01	14	-0.06	0.04	12
DOC	-0.23	0.44	33	0.39	0.45	49
Chl <i>a</i>	0.21	-0.17	18	0.16	0.44	46
COND	-0.85	0.16	83	0.75	-0.24	76
Turb	0.66	0.07	71	-0.43	0.36	45
ANC	-0.81	-0.31	86	0.28	-0.36	57

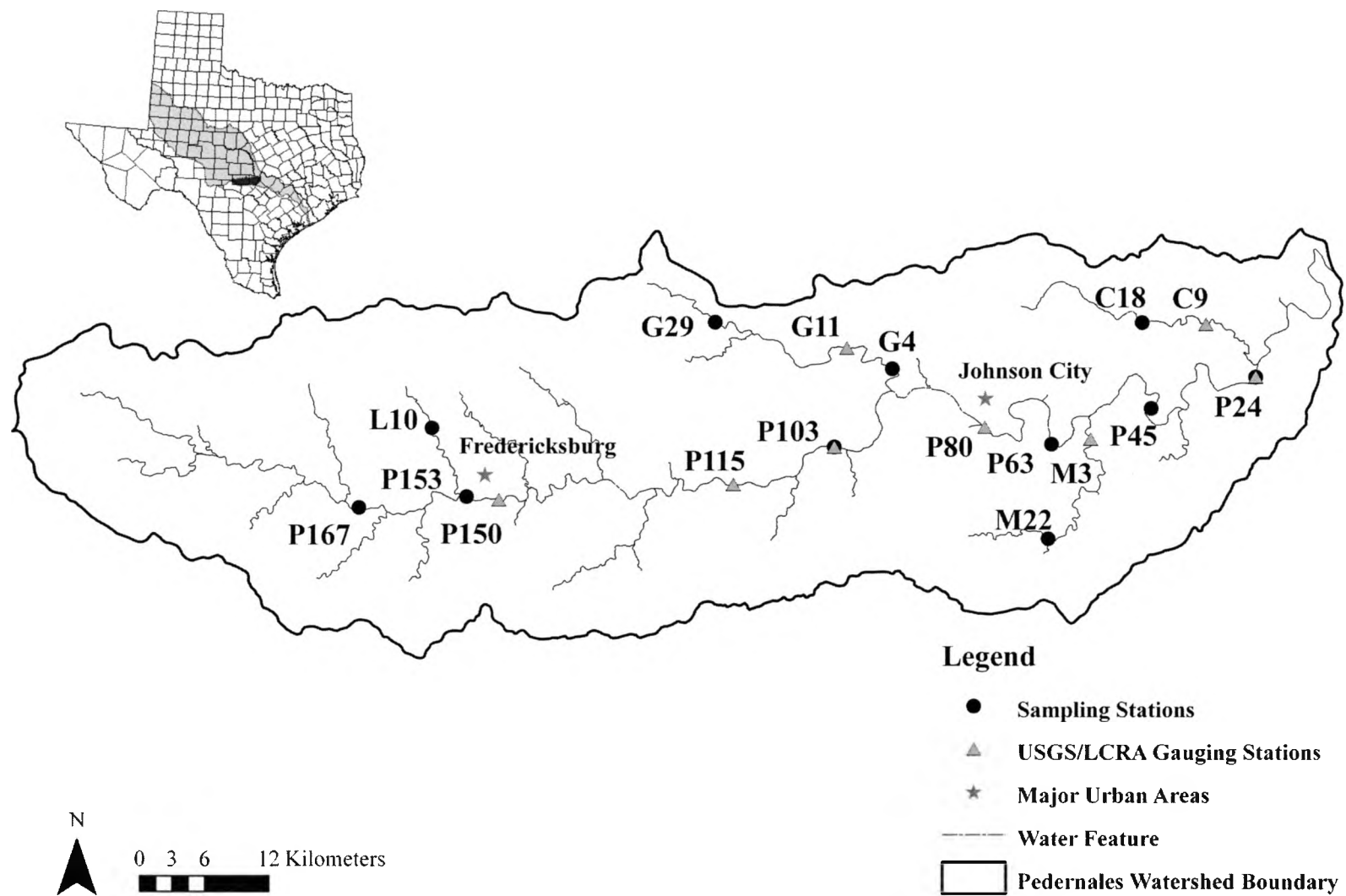


Figure 1. Location of study area and sampling stations in the Pedernales River watershed, Texas. Stations identified by first letter of water feature (i.e., Pedernales River (P); Cypress (C), North Grape (G), Live Oak (L), and Miller (M) Creeks) and river kilometer.

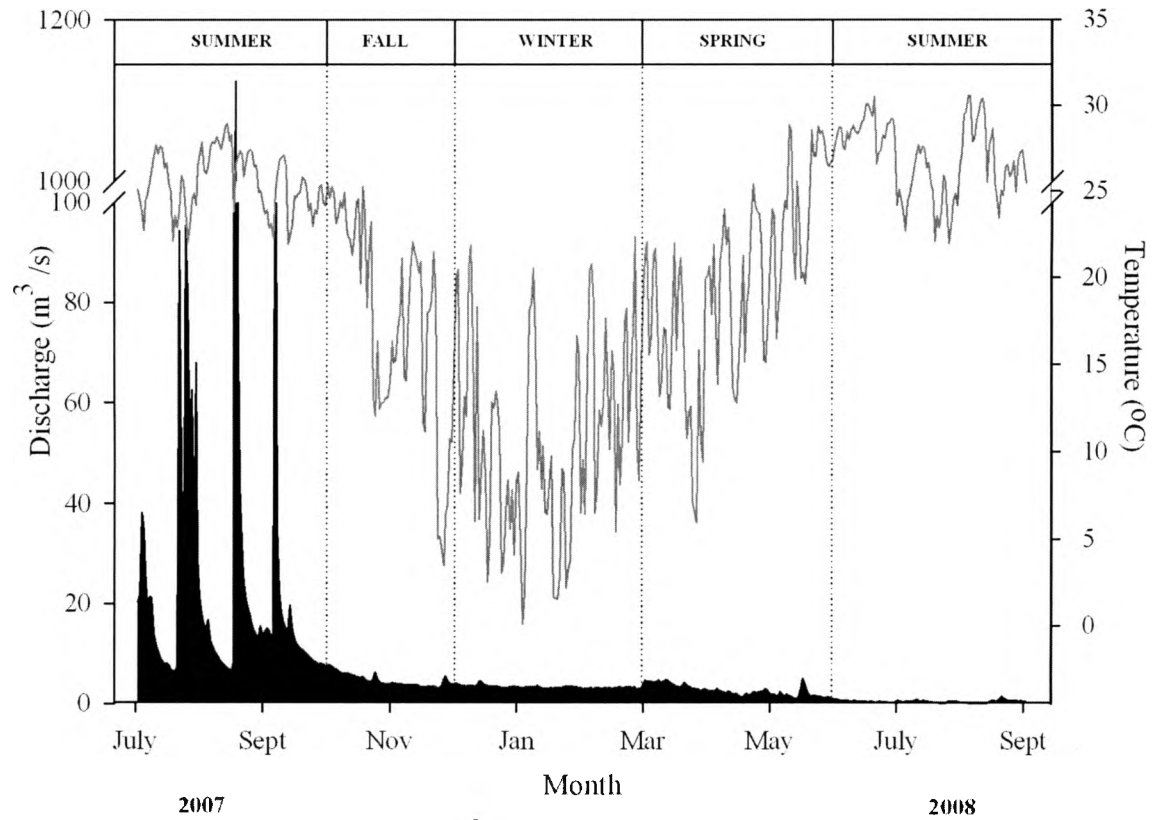


Figure 2. Mean daily discharge (m³/s) and mean daily air temperature (°C) at the central region of the Pedernales River watershed (sample station P80, Figure 1). Discharge data taken from U.S. Geological Survey discharge data, and air temperature data taken from Lower Colorado River Authority hydromet data collected from July 2007 through August 2008.

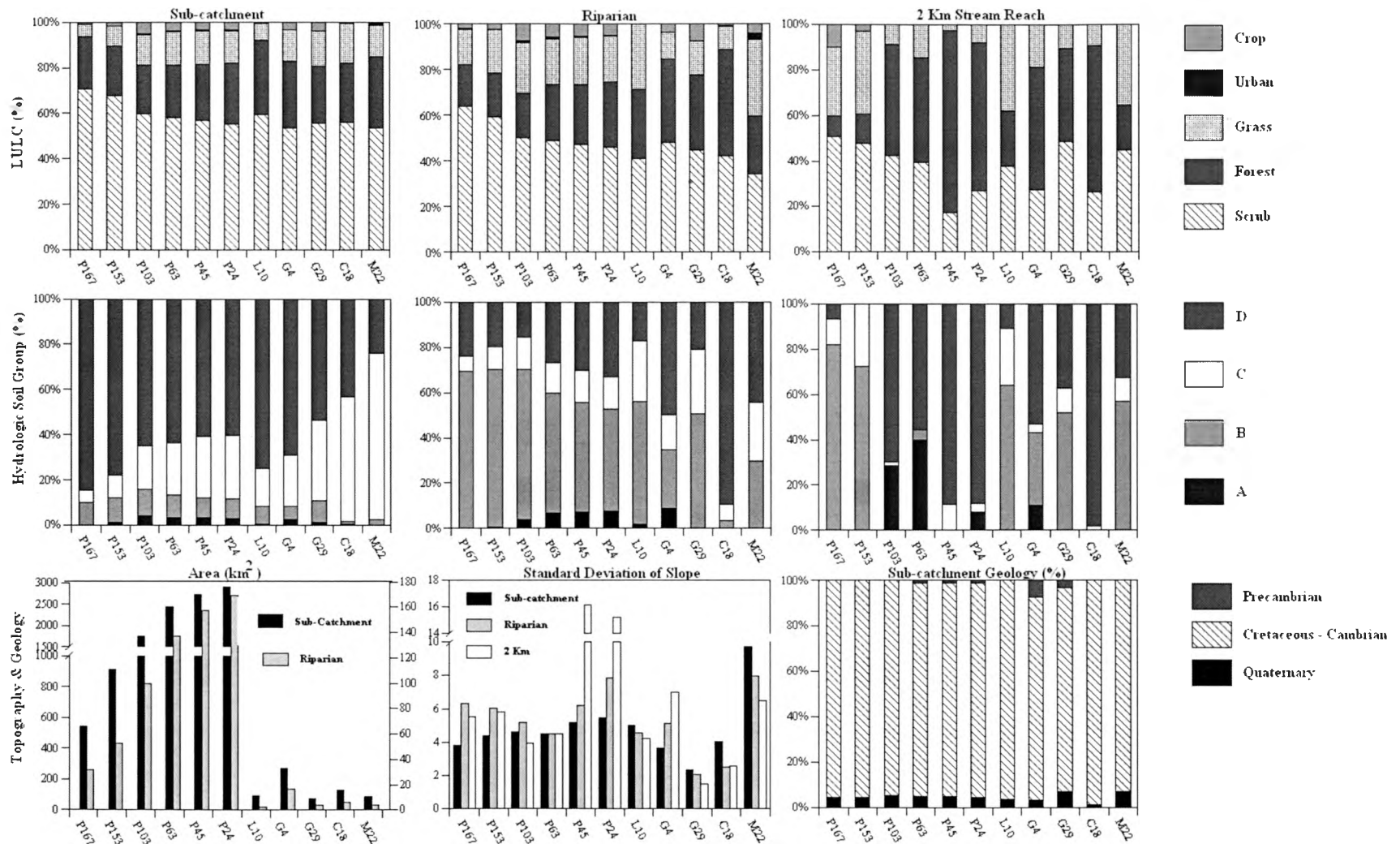


Figure 3. Sub-catchment, riparian, and 2 km stream reach landscape features of the 11 sampling stations within the Pedernales River watershed.

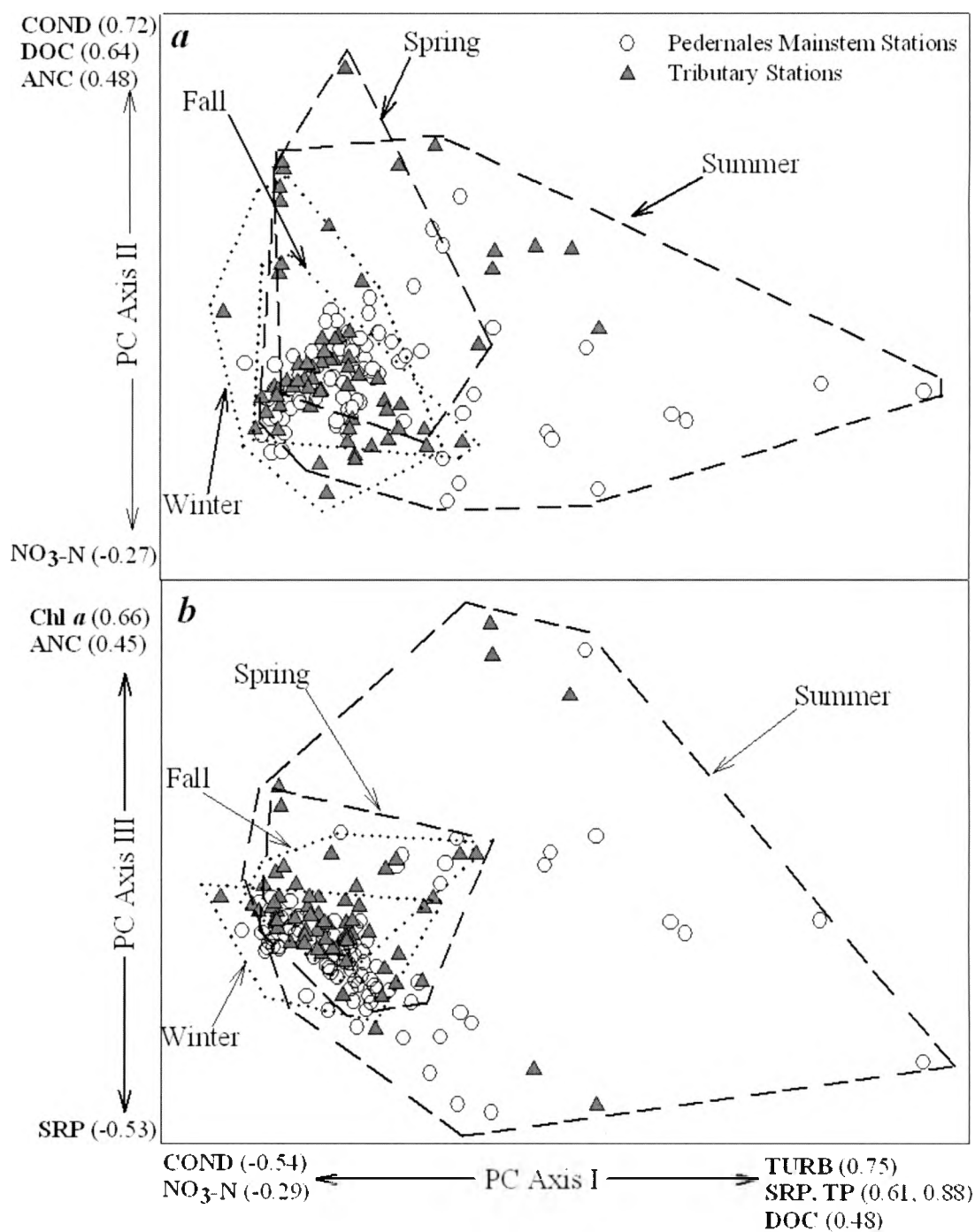


Figure 4. Principal components analysis (PCA) ordination diagram illustrating observations from all sampling stations along (a) PCA axis I and II, and (b) PCA axis I and III. Eigenanalysis determined that 62% of the variance in the data set was explained by the first three principal component axes. Variable loadings are identified adjacent to water chemistry parameter on either axis. The dashed lines encompass the observations by spring and summer season, and dotted lines encompass fall and winter.

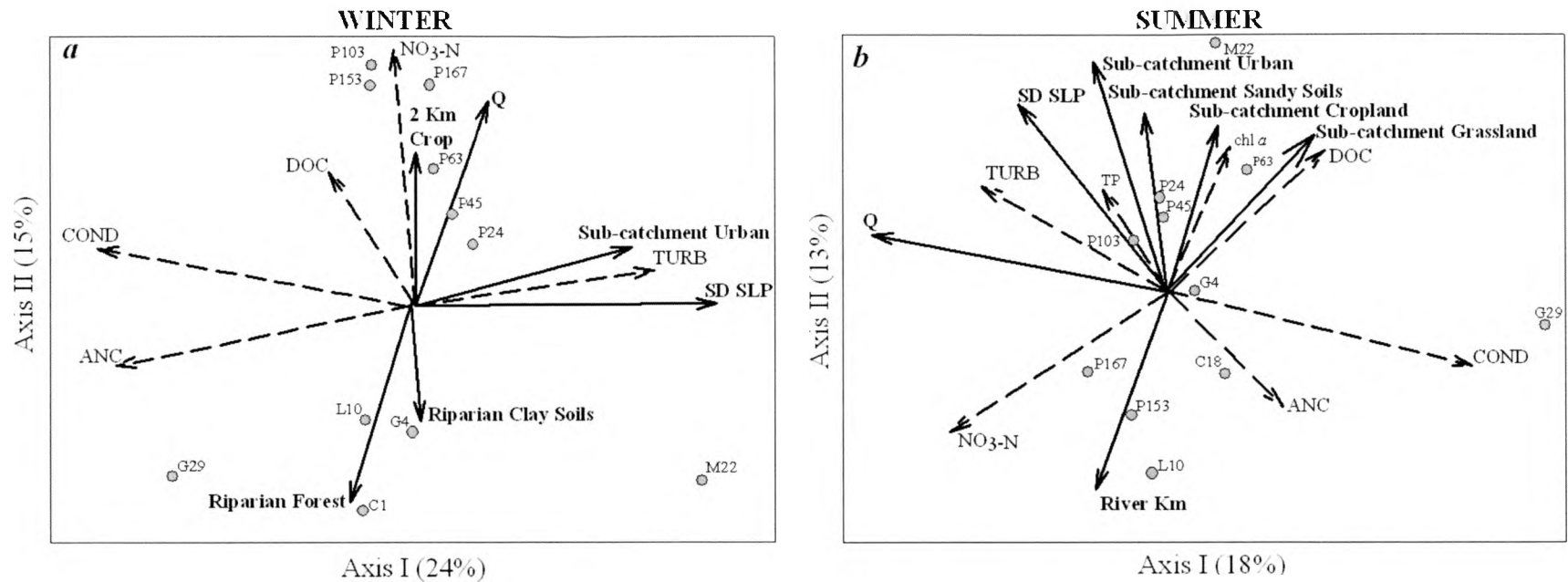


Figure 5. Redundancy analysis (RDA) ordination diagram illustrating landscape-water chemistry associations and mean sampling station scores across (a) fall-winter and (b) spring-summer. Solid lines indicate loadings of independent variables, dashed lines are dependant response variables, and grey circles indicate sample stations. A Monte Carlo test found the overall model to be significant ($p < 0.0001$) across both seasons. Eigen analysis determined that 39% of the variation in winter water chemistry, and 31% of the summer water chemistry was explained by the first two axes.

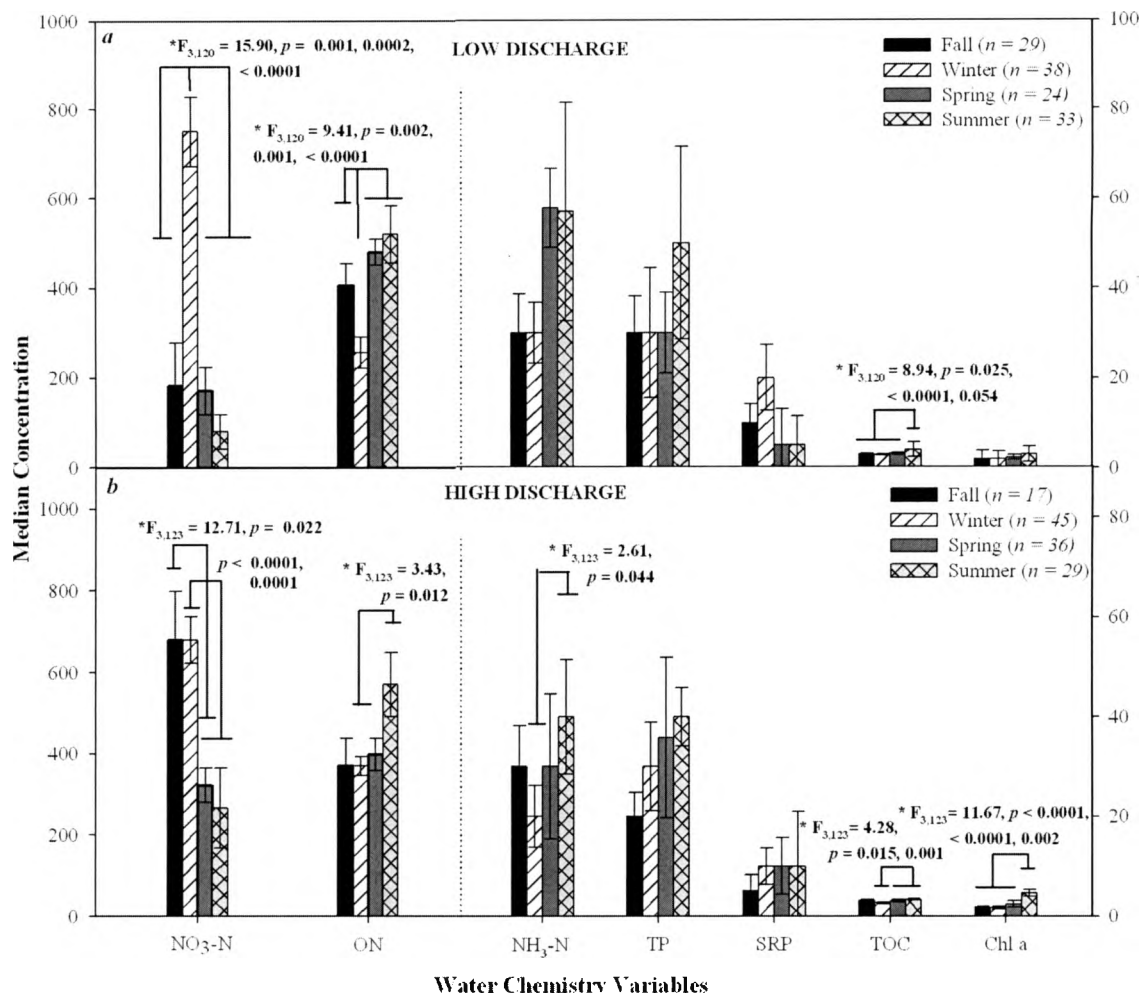


Figure 6. Median values (± 1 SE) for selected water chemistry variables from sampling stations P103 and P80. All concentrations are $\mu\text{g/L}$ except for TOC, which is illustrated in mg/L . Dashed line delineates y-axis scale. Significant differences are identified under connected bars. F value is from one-way ANOVA results, and p value is from Tukey's multiple comparison test. (a) Samples taken at an instantaneous discharge below long-term median flows; (b) samples taken at an instantaneous discharge greater than long-term median.

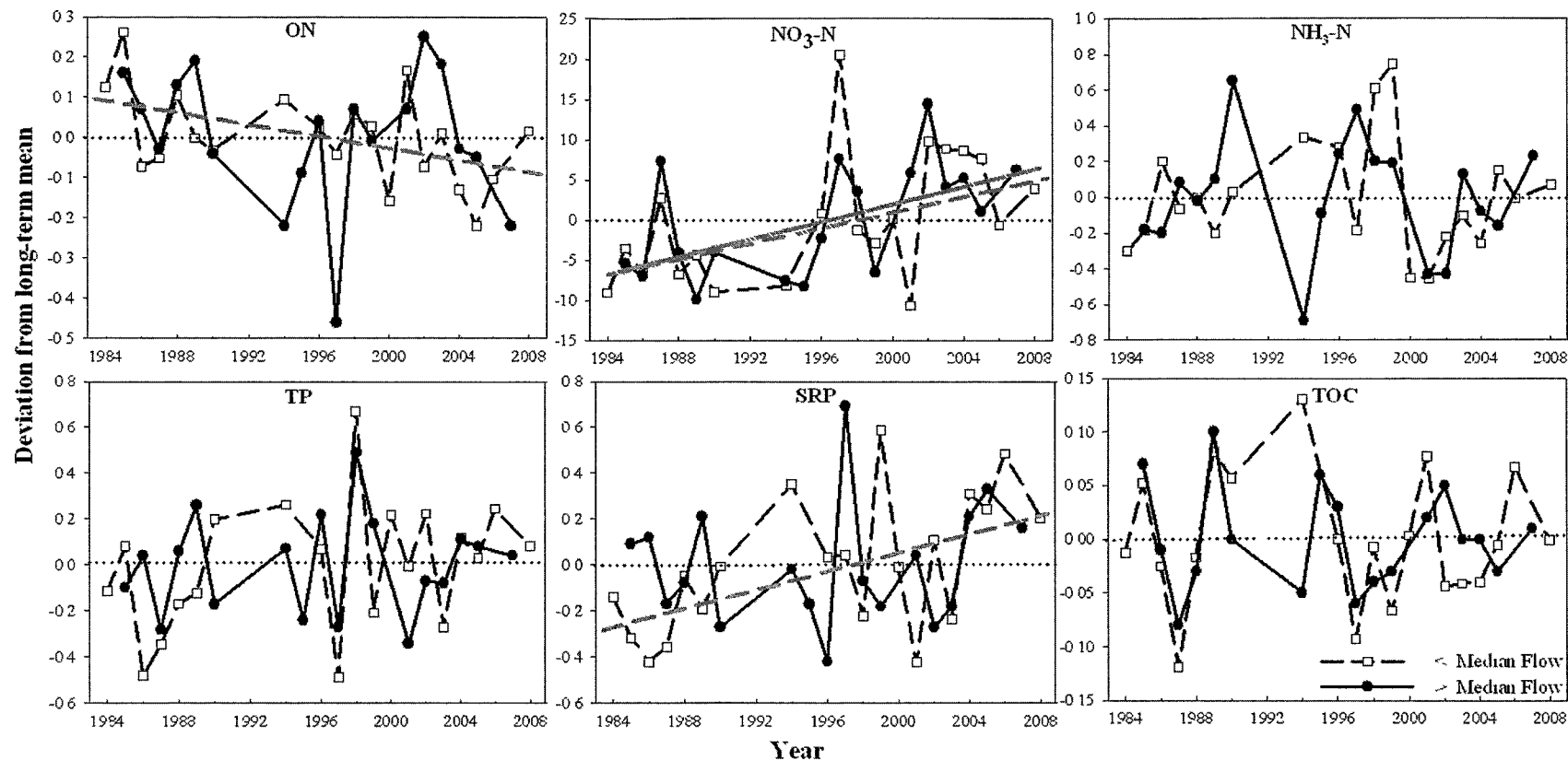


Figure 7. Trends in nutrient concentrations from 1984 – 2008 at sampling stations P103 and P80. Dotted line represents long-term mean (0.0) and points are the yearly average concentrations deviation from long-term mean. Dashed lines correspond with samples taken below long-term median flow, and solid line represents samples above long-term median flow. Dashed and solid slope lines represent significant trends. Long-term mean concentrations during low and high-discharge conditions are: 469 and 427 $\mu\text{g/L}$ (ON), 458 and 600 $\mu\text{g/L}$ (NO₃-N), 71 and 49 $\mu\text{g/L}$ (NH₃-N), 60 and 43 $\mu\text{g/L}$ (TP), 27 and 26 $\mu\text{g/L}$ (SRP), 4 and 3 mg/L (TOC).

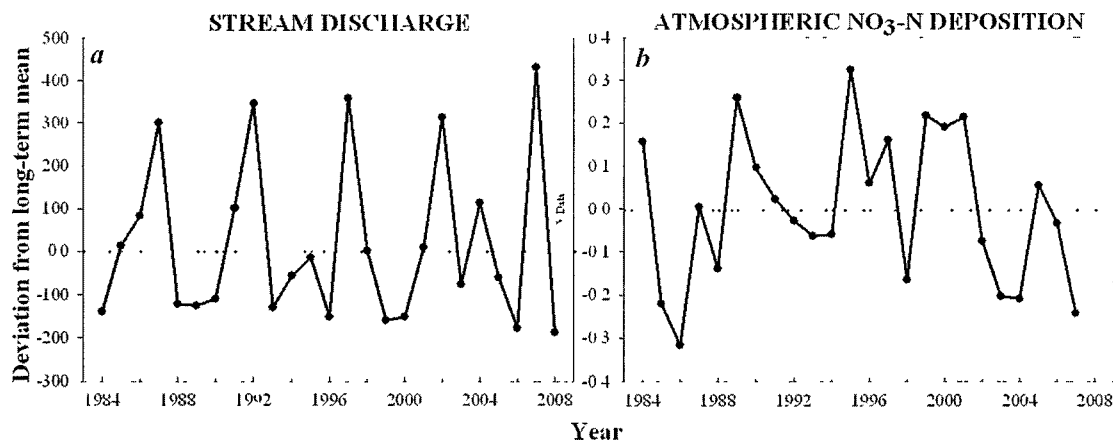
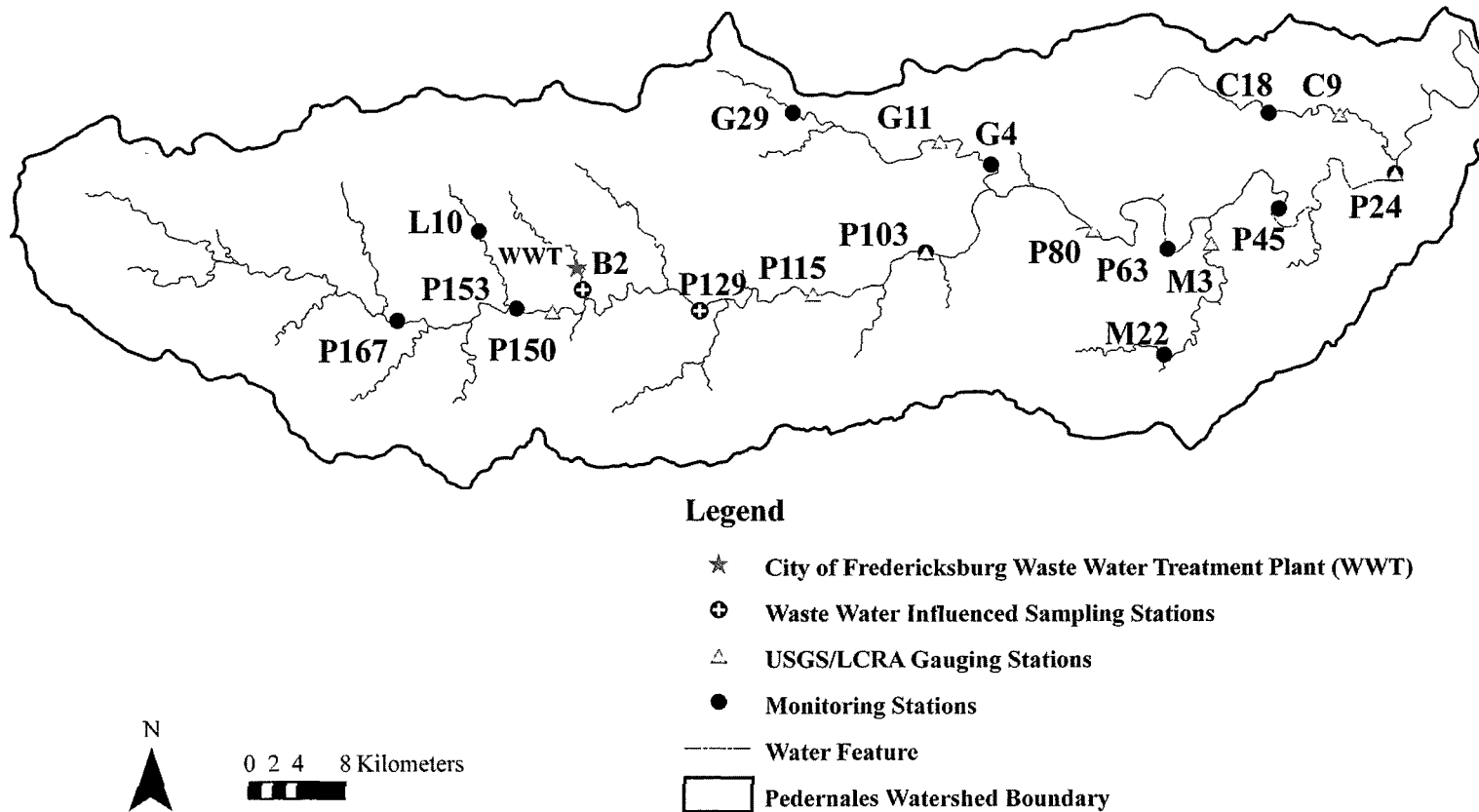
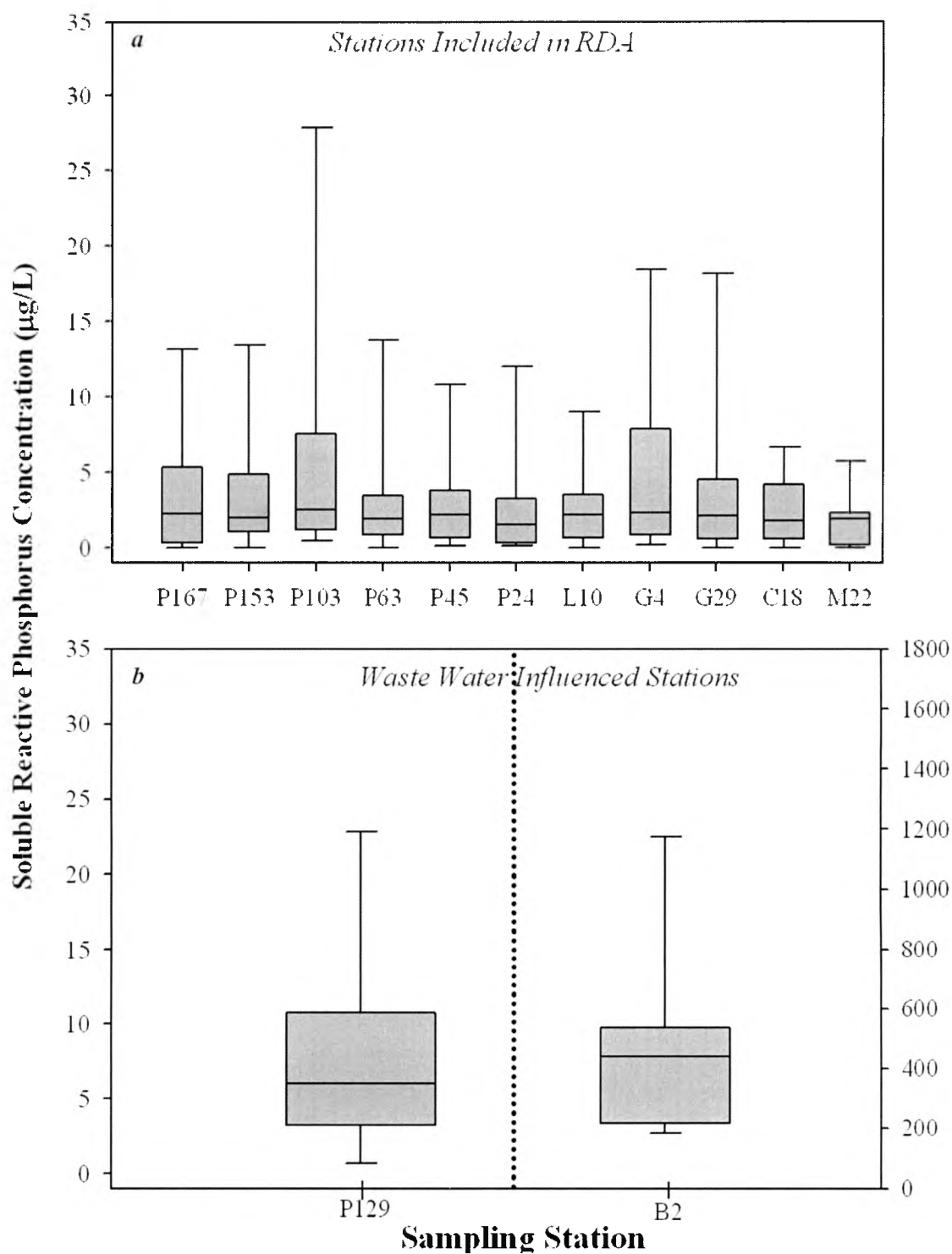


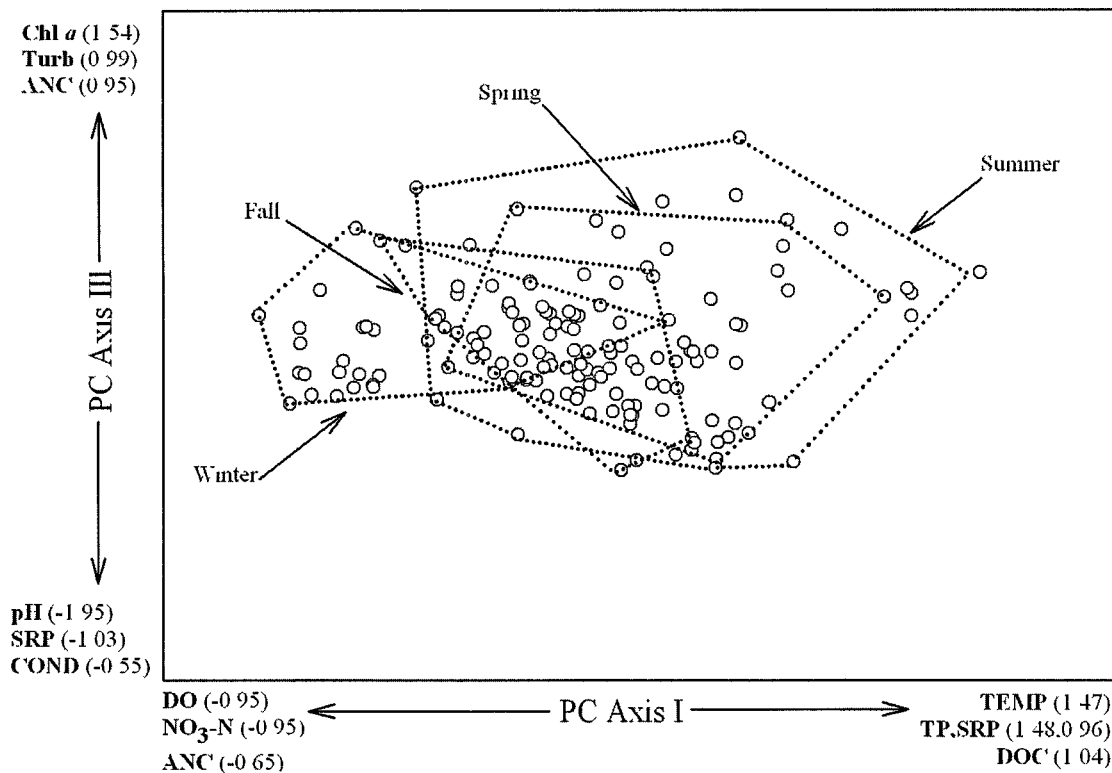
Figure 8. Trends in stream discharge and atmospheric NO₃-N deposition from 1984-2008. (a) Stream discharge data taken from U.S. Geological Survey discharge data (P80). (b) Atmospheric NO₃-N data taken from National Atmospheric Deposition Program, average annual NO₃-N concentration in precipitation in Sonora, TX (approximately 200 km northwest of study area). Dotted line represents long-term mean (7.16 m³/s, 1022 μg/L, respectively), and points are yearly average deviation from long-term mean.



APPENDIX A.1. Location of sampling stations associated with the City of Fredericksburg Waste Water Treatment Plant. Pedernales River station (P129) is located approximately 10 river kilometers downstream of tributary receiving waste water effluent (Baron's Creek (B2)).



APPENDIX A.2. Box-plot diagram illustrating soluble reactive phosphorus concentrations at (a) sampling stations included analysis and (b) sampling stations associated with wastewater effluent (dotted line delineates y-axis scale). The horizontal line inside boxes represents sampling station mean and outer box edges represent the 25th and 75th percentile. Whiskers represent the 5th and 95th percentile.



APPENDIX B. Principal components analysis (PCA) ordination diagram showing observations from all sampling stations. Eigenanalysis determined that 57% of the variance in all water chemistry measures was explained by the first three principal component axes. PC axis I and III were used to illustrate water chemistry associations as identified relationships were more pertinent in relation to study questions, and because PC axis III explained only slightly less variation than PC axis II (14 and 16%, respectively). Variable loadings are identified adjacent to water chemistry parameter on either axis. The dotted lines encompass the observations by season.

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