NITORGEN AND PHOSPHORUS TRANSPORT IN AN URBAN WATERSHED

By

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This work is dedicated to my mom

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of Thesis Presented to the Graduate School
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Non-point source pollution is the dominant pathway of nitrogen (N) and phosphorus (P) transport in agricultural, urbanized, and rapidly urbanizing watersheds. We used monthly concentrations data of inorganic and organic forms of N and P in stream waters draining different sub-basins, ranging in size from 19 to 350 km^2, of the Alafia River Watershed (total drainage area: 1085 km^2), which ultimately drains to Tampa Bay Estuary, to understand N and P transport. The sub-basins were classified based on the percentage of urban land use as three developed (18–24% residential, 1–14% built up) and two undeveloped (3–11% residential, 1–3% built up). Urban land use at two mainstem stations that drained 80–99% of the watershed was 16–17% residential and 3% built up. During 1991–2009, total N concentrations ranged from 0.8 to 2.4 mg L^{-1} and were greatest in stream waters draining developed (1.7–2.4 mg L^{-1}) than undeveloped (0.8–1.2 mg L^{-1}) sub-basins. Inorganic N (primarily NO_3-N) was the dominant form in streams draining developed sub-basins while organic N was greater in streams draining undeveloped sub-basins. Total P concentrations ranged from 0.6 to 3.9 mg L^{-1} and were not different among developed (0.8–3.9 mg L^{-1}) and undeveloped (0.6–0.9 mg L^{-1}) sub-basins. Of total P, 70–90% was dissolved reactive P while other P forms were 10–30% of total P in both developed and undeveloped sub-basins. The increasing total N and decreasing total P

concentrations trends at the mainstem station draining 89% of the watershed over the 19-year period suggests that the development of the watershed resulted in increasing N but not P concentrations in streams. We suggest that the BMP's to reduce N loss from urban land uses in three developed sub-basins (with total N of 1.7–2.4 mg L^{-1}) may yield greater reductions in N concentrations at watershed outlet (i.e. mainstem) to achieve EPA proposed numeric criteria of total N concentration of 1.798 mg L^{-1}. On the other hand, due to P rich geology and discharge from the wastewaters, most developed and undeveloped sub-basins had greater total P concentrations (0.8–3.9 mg P L^{-1}) than EPA proposed numeric total P value of 0.739 mg L^{-1} indicating that BMP's should focus on reducing P loss from phosphate rock mined sub-basins and reduce P inputs from wastewater.

CHAPTER 1
INTRODUCTION

Eutrophication

Eutrophication is a broad term used to describe enhanced phytoplankton growth in water bodies such as lakes, rivers, reservoirs, and estuaries that receive excess nitrogen (N) and phosphorus (P) from the landscape (Jansson and Dahlberg, 1999; Paerl, 2009). The consequences of eutrophication include hypoxia, acidification of natural waters, degradation of coastal waters including increased episodes of noxious algal blooms, and reductions in aquatic macrophyte communities often leading to substantial shifts in ecosystem structure and function (Carpenter et al., 1998; Dodds et al., 2009). In the US, eutrophication is one of the greatest threats to the health of the estuaries. For example, Bricker et al. (1999) in their assessment of 138 estuaries reported that nearly 60% of estuaries exhibited moderate to severe eutrophic conditions. In Florida, threshold concentrations of 1.20–1.79 mg N L^{-1} and 0.107–0.739 mg P L^{-1} have been proposed for stream waters in three of four regions of Florida (EPA, 2010).

The phytoplankton growth in waterbodies is dependent upon the N: P ratio. For example, total N: P ratio of 16:1 is suggested for optimum phytoplankton growth, termed as Redfield Ratio (Redfield, 1934). An N: P ratio of <16:1 is indicative of N limitation while >16:1 indicates P limitation. In a review from 40 studies, Koerselman and Meuleman, (1996) reported that at an N: P ratio of >16, P would be a limiting nutrient and at N:P <14, N would be limiting, and at intermediate values (14–16) either N and/or P would be limiting nutrients for phytoplankton growth. In the Tampa Bay estuary, monthly water quality concentrations data from 1981–2004 showed that the N: P ratio in the stream waters was about 5:1 suggesting that this water body is N limited (Dixon et al., 2009). Further, it has been suggested that the loss of seagrass beds in the Tampa Bay estuary is a direct consequence of N loading to the Bay from several point and non

point sources (TBEP, 2009). Therefore, source control on N needs greater attention than P, for controlling eutrophication in the Tampa Bay. Although, recent research has suggested that controls on both N and P transport might be needed to control eutrophication in freshwater-marine continuum (Conley et al., 2009; Paerl, 2009).

Nitrogen and Phosphorus in the Environment

Nitrogen

The largest global pool of N exists as dinitrogen gas (N_2) comprising up to 78% in the lithosphere. However, only specialized microbes and cyanobacteria with the enzyme nitrogenase can directly use N_2 via N fixation, while for >99% of the organisms, N_2 is made available by inorganic N fertilizers using Haber-Bosch process where N_2 is converted to ammonia (NH_3). Living organisms utilize inorganic N in the metabolic processes and convert it into organic N (ON) forms such as amino acids, proteins, and nucleic acids. After the organisms die, micro-organisms break down ON to ammonium (NH_4^+) which can be oxidized to NO_3^- via nitrification. Finally, the denitrification process, in which micro-organisms oxidize organic matter using NO_3^- as electron acceptor under reduced conditions close the N cycle by converting NO_3^- back into N_2 (Galloway et al., 1996). Therefore, in different steps of N cycle, NO_3^-, NH_4^+, and ON forms are either produced or consumed while the excess amount of these forms at each step has the potential to be transported to waterbodies resulting in water quality deterioration.

Phosphorus

Like N, P in waterbodies exists in several combinations of organic and inorganic forms. Haygarth and Sharpley (2000) suggested a physicochemical classification (i.e. filtration and chemical methodology) to differentiate inorganic and organic P forms in water. According to this classification, P can be divided into two main forms: dissolved (<0.45 µm) and particulate (>0.45 µm). Dissolved P can be further divided into dissolved reactive P (DRP: orthophosphate)

and dissolved unreactive P (DUP: organic P forms such as sugar phosphates, mononucleotides, DNA, RNA, and phospholipids). Similarly, particulate P can be divided into particulate reactive P (PRP: P sorbed on sediments, Fe, Al, or Ca oxides) and particulate unreactive P (PUP: P sorbed on mineral-humic acid complexes) (Toor et al., 2004). Dissolved and particulate P forms in water bodies change from one form to another in response to a variety of environmental and biological responses. For example, microbial decomposition or chemical desorption can convert P from particulate to dissolved forms. Similarly organisms can take up dissolved P and transform them into particulate P forms. As a result, P in the waterbodies is present in organic and inorganic forms and is continually recycled.

Sources of Nitrogen and Phosphorus in Watersheds

Anthropogenic activities such as application of fertilizers, manures, industrial effluents, and wastewater discharge are the major known sources of N and P in watersheds (Anisfeld et al., 2007; Russell et al., 2008). Therefore, the inputs of N and P are greater in human dominated land uses (agricultural and urban) as compared to relatively undeveloped land areas such as natural forests (Boyer et al., 2002; Kaushal et al., 2008; Russell et al., 2008).

Nutrient input sources can be divided into “point sources” such as wastewater and industrial effluents and “non-point sources” such as runoff and leaching from urban and agricultural areas. With the implementation of the Clean Water Act in the late 20th century, N and P concentrations from point sources have been substantially reduced in the US (Howarth et al., 2002). However, non-point source pollution is dominant in most of the watersheds in the US and elsewhere. Non-point source pollution is difficult to control because the pollution sources cannot be attributed to one particular discharge location but rather to a diffused landscape (Rhodes et al., 2001). For example, since 1987, the United States Department of Agriculture Conservation Reserve Program (CRP) has distributed $29.7 billion to agricultural land owners to

implement conservation practices to reduce soil loss, restore wetlands, and conserve forested areas (USDA, 2006). However, these conservation measures showed a little evidence of improvements in stream water quality at broad spatial scales as a greater emphasis of this program was to reduce soil erosion to control nutrient losses, which was not successful in controlling dissolved N losses (Boesch et al., 2001; Meals, 1996). Secondly, it was assumed that all areas in the landscape contribute uniformly to nutrient loads, which resulted in less favorable outcomes of reducing nutrient losses to water bodies.

Recent research has provided insights about contribution of various non-point sources to nutrient loading in watersheds. For example, Poe et al. (2006) estimated that storm water runoff contributes 63% of annual N loads in the Tampa Bay (Fig. 1-1). They further estimated that in the storm water runoff, the residential areas were the major N contributors (20%) followed by pasture/rangelands (15%), intensive agriculture (12%), and mining lands (6%). The second most important source of N in Tampa Bay is atmospheric deposition (21%), while the contribution of point sources such as domestic wastewater (9%) and industrial wastewaters (3%) is comparatively lower than the non-point sources. The reduction of non-point source pollution is urgently needed to protect and conserve water resources (USEPA, 2002). In case of P, such a detailed analysis of various sources is lacking, however, it can be construed that the contribution of different land uses to storm water runoff may be different, with higher contribution of P from mined lands and wastewater discharges. In addition to different sources in the non-point category, we also know that in each watershed, there are “hot spot” areas, termed as variable source areas, which contribute a majority of nutrient losses (Poe et al., 2006; Diebel, 2009). Therefore, a first step in controlling non-point source pollution is to develop a quantitative understanding of their sources (i. e. hot spot areas) in the landscape followed by using best

management practices (BMPs) to control nutrient losses from these areas (Diebel et al., 2009; Maxted et al., 2009). For example, Diebel et al. (2009) reported that targeting 10% watersheds in Wisconsin, US decreased total P loads by 20% for the entire state. Therefore, the conservation programs targeting the hot spot areas present an effective way to control nutrient losses and improve water quality in a watershed while using less resources rather than attempting to use BMP's for an entire watershed. Secondly, understanding how land uses impact nutrient losses can help to unravel mechanisms of nutrient transport, which can lead to fine-tune BMP's to reduce nutrient losses from land to water and protect water resources.

Research Objectives

In the Southern US, population is anticipated to increase from approximately 8 million in 1992 to 22 million in 2020 and 33 million in 2040 (Wear, 2002). Florida is one of the rapidly developing states in the US and has serious water quality problems such as eutrophication of coastal waters (Dame et al., 2002). Therefore, it is important to assess the impact of anthropogenic activities on water quality of coastal waters. Very little is known about N and P fate and transport in urban watersheds in Florida, which have a high proportion of sandy soils, high ground water table, and altered hydrology due to storm water retention ponds. The Alafia River Watershed (1085 km^2) which drains into the Tampa Bay estuary was our study site to understand the N and P transport as several years of historic water quality data was available. Secondly, this watershed represents a typical urbanizing watershed in the region with diverse mix of urban, agricultural, and mined land uses. The main objectives of this research are presented below along with specific aims for each objective.

Objective 1. Evaluation of Nitrogen Concentrations in Different Sub-basins of the Alafia River Watershed.

Aim 1a. Determine how different sub-basins influence concentrations of inorganic and organic N forms.

Aim 1b. Evaluate the influence of low (dry season) and high (wet season) flow conditions on stream N concentrations in different sub-basins.

Aim 1c. Determine the long term trends of N concentrations in different sub-basins.

Objective 2. Evaluation of Phosphorus Concentrations in Different Sub-basins of the Alafia River Watershed.

Aim 2a. Determine how different sub-basins influence concentrations of P forms.

Aim 2b. Evaluate the influence of low (dry season) flow and high (wet season) flow conditions on stream P concentrations in different sub-basins.

Aim 2c. Determine the long term trends of P concentrations in different sub-basins.

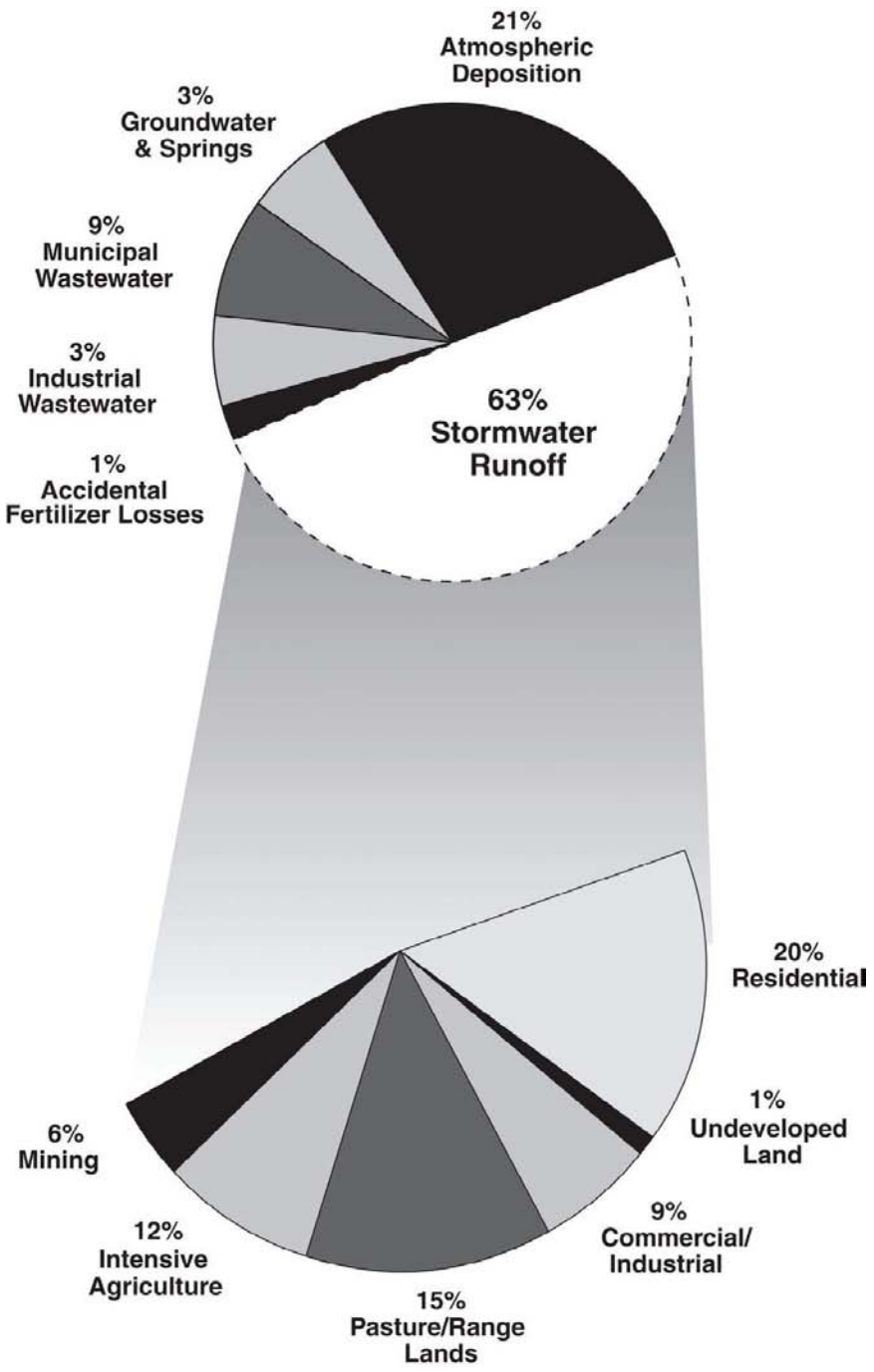

Figure 1-1. Estimated sources of nitrogen in the Tampa Bay (Adapted from Poe et al., 2006).

CHAPTER 2
STUDY SITE DESCRIPTION

Location

Alafia River Watershed is located in the central Florida and drains 1085 km^2 of land area (Fig. 2-1). The headwaters of the Alafia River originate from the swamp and prairie lands of Polk County and extend 38.6 km long flowing west into lower Hillsborough Bay, ultimately discharging into Tampa Bay Estuary (SWFWMD, 2007). The soils in the watershed are sandy, with moderate to slow infiltration and are dominated by Myakka, Winder, Zolfo, Lake, and Chandler soil groups (USDA, 2010).

Climate

The climate in the area is humid subtropical, with an annual mean temperature of 22.3˚C. Long term (1891–2009) annual average precipitation was 120 cm; ~60% of precipitation occurred during a four-month period from June to September while 40% of the rainfall occurred during eight months period from October to May (Florida Climate Center, 2009). Therefore, a water year is divided into wet season i.e. high flow conditions from June–September and dry season i.e. low flow conditions from October–May.

Sub-basins of the Alafia River Watershed

Two mainstem stations namely Bell Shoals and Alafia drain 80 to 99% of the watershed (Fig 2-1). Bell Shoals drains 89% of the watershed and includes discharge from five sub-basins i.e. North Prong, South Prong, and English Creek, Turkey Creek, and Fishhawk Creek. While the Alafia station drains 99% of the watershed and include discharges seven sub-basins including five from Bell Shoals station and Bell Creek and Buckhorn Creek. We grouped the FLUCCS codes at level IV into residential, built up, agricultural, pasture, mined, and forest land uses (Table 2-2). The commercial, industrial, institutional, and transportation (such as roads) were

included under the built up land use. On the other hand, residential land use included the low, medium, and high density residential. In this study, the residential and built up land uses were considered as urban land use.

Overall, at two mainstem stations (Alafia and Bell Shoals), watershed land use was dominated by mined (32–34%), followed by forest (19%), residential (16–17%), built up (3%), pasture (11%), and agricultural (8–9%) (SWFWMD, 2007; Table 2-1). We grouped different sub-basins of the Alafia River Watershed using percent residential land use into two categories: 1) three developed (18–24% residential land use) and 2) two undeveloped (3–11% residential land use). A detailed description of sub-basins is given below.

Developed Sub-basins

Turkey Creek

In 2007, Turkey Creek had 20% residential, 3% built up, 24% agricultural, and 16% pasture land use (Fig. 2-2; Table 2-1). Other land uses in the sub-basin include 12% forest, 17% reclaimed, and 2% mined lands. Turkey Creek was under active mining operations during 1990, however, all of the mining land use in the sub-basin was reclaimed by 2007 (Fig. 2-2). Other significant land use changes in the sub-basin include a 9% increase (from 11% to 20%) in residential and 9% decrease (from 25% to 16%) in pasture land use during 1990–2007. In contrast to changes in mined and residential land use, the percent agricultural land use remained similar at 22–24% in the sub-basin during 1990–2007. One domestic wastewater treatment plant discharges 0.13 m^3 sec^{-1} of wastewater with total N and total P concentration of 2.25 mg L^{-1} and 0.36 mg L^{-1}, respectively in this sub-basin (NPDES, 2009).

English Creek

In 1990, the land use in the English Creek was 38% pasture, 19% agricultural, 10% residential, 1% built up (Fig. 2-3). The sub-basin has undergone significant land use changes

during 1990–2007. For example, the residential land use in the sub-basin increased by 11% (from 10% to 21%) followed by 13% increase (from 1% to 14%) in built up during 1990–2007. The increase in residential and built up land use has occurred at the expense of pasture land use, which has decreased by 24% from 38% in 1990 to 16% in 2007 (Fig. 2-3). During 1990–2007, the forest and agricultural land use remained similar at 17–19% and 25–28%, respectively.

Florida Department of Health has indentified 943 housing units on septic tanks in this sub-basin (Florida Department of Health, 2009). In addition, several small animal feed additive producing plants discharge wastewater in the sub-basin (NPDES, 2009).

North Prong

North Prong is the largest sub-basin draining 350 km^2 of the Alafia River Watershed. Significant changes in the residential, pasture, and mined land use have occurred in this sub-basin during 1990–2007. In 1990, North Prong had 13% residential, 13% pasture, and 44% mined land use (Fig. 2-4; Table 2-1). While in 2007, there was 39% mined, 18% residential, 6% built up, 5% pasture, and 4% agricultural land uses (Fig. 2-4; Table 2-1). In this sub-basin, one domestic wastewater treatment plant discharges ~0.35 m^3 sec^{-1} of wastewater with total N and P concentrations of 1.19 mg L^{-1} and 3.1 mg L^{-1}, respectively (http://cfpub2.epa.gov/npdes/index.cfm).

Mined land use can be divided into four categories: active mine lands, reclaimed mined lands, lands owned by mine interests that are yet to be mined, and lands owned by mine interests that cannot be mined (SWFWMD, 2007). However, the Florida land use classification system does not discriminate among these four mined land uses categories.

Undeveloped Sub-basins

South Prong

South Prong is the second largest sub-basin that drains 277 km^2 of the Alafia River Watershed. In 1990, 93% area in the South Prong sub-basin was under mining operations (Fig. 2-5). However, reclamation of the mined land occurred during 1990–2007. For example, in 2007, only 66% of the sub-basin was under mined land use (Fig. 2-5; Table 2-1) while the remainder was forest (15%), pasture (9%), and agriculture (4%). In contrast to North Prong, South Prong is less developed with residential land use of 3%. Several small industrial wastewater plants (phosphate mines) discharge wastewater into South Prong during high rainfall events.

Fishhawk Creek

In 1990, Fishhawk Creek was undeveloped with 1% residential, 43% forest, 29% pasture, and 16% mined land use (Fig. 2-6). All of the mined land in the sub-basin has been reclaimed and comprised 10% of the sub-basin in 2007 (SWFWMD, 2007). During 1990–2007, residential land use increased from 1% to 11% (Fig. 2-6; Table 2-1) while other land uses were 11% agricultural and 23% pasture land.

Table 2-1. Station characteristics and associated land uses in the various sub-basins on the Alafia River Watershed

Sub-basin	Station	Sampling location		Drainage area		Land Use in 2007					
		Lat	Long	km^2	%	Residential	Built up	Agricultural	Pasture	Forest	Mined
					Mainstem Stations						
Alafia	2301718	27.87	–82.32	1072	99	17	3	8	11	18	32
Bell Shoals	2301638	27.86	–82.26	974	89	16	3	8	12	18	33
					Developed						
English Creek	-†	27.93	–82.06	99	9	21	14	19	23	25	3
Turkey Creek	-†	27.91	–82.18	128	13	20	3	24	16	12	0
North Prong	2301000	27.86	–82.13	350	32	18	6	4	5	16	39
					Undeveloped						
South Prong	2301300	27.86	–82.13	277	26	3	1	4	9	15	66
Fishhawk Creek	†	27.85	–82.24	70.6	7	11	3	14	23	32	0

-† USGS station not present

Table 2-2. Grouping of FLUCCS codes into major land uses (Source: SWFWMD, 2007).

Land Use	Description	FLUCCS Code
Residential	Low density	1100
	Medium density	1200
	High density	1300
Built Up	Commercial and services	1400
	Industrial	1500
	Institutional	1700
	Transportation	8100
	Communications	8200
	Utilities	8300
Agriculture	Row crops	2140
	Tree crops	2200
	Feeding operations	2300
	Nurseries and vineyards	2400
	Specialty farms	2500
	Fish farms	2550
	Other open lands	2600
Pasture	Pastureland	2100
Forest	Herbaceous	3100
	Shrubs and brush land	3200
	Mixed rangeland	3300
	Upland coniferous forest	4100
	Pine woodlands	4110
	Upland hardwood forests	4200
	Hardwood conifer mixed	4340
	Tree plantations	4400
	Wetland hardwood forests	6100
	Cypress	6210
	Wetland forested mixed	6300
	Freshwater marshes	6410
	Salt water marshes	6420
	Wet prairies	6430
	Emergent aquatic vegetation	6440
	Extractive	1600
Mined	Reclaimed lands	1650
Reclaimed	Recreational	1800
Recreational	Golf courses	1820
	Open lands	1900
	Streams and waterways	5100
Other	Lakes and Reservoirs	5200, 5300
	Bays and estuaries	5400

FLUCCS: Florida Land Use and Cover Classification System

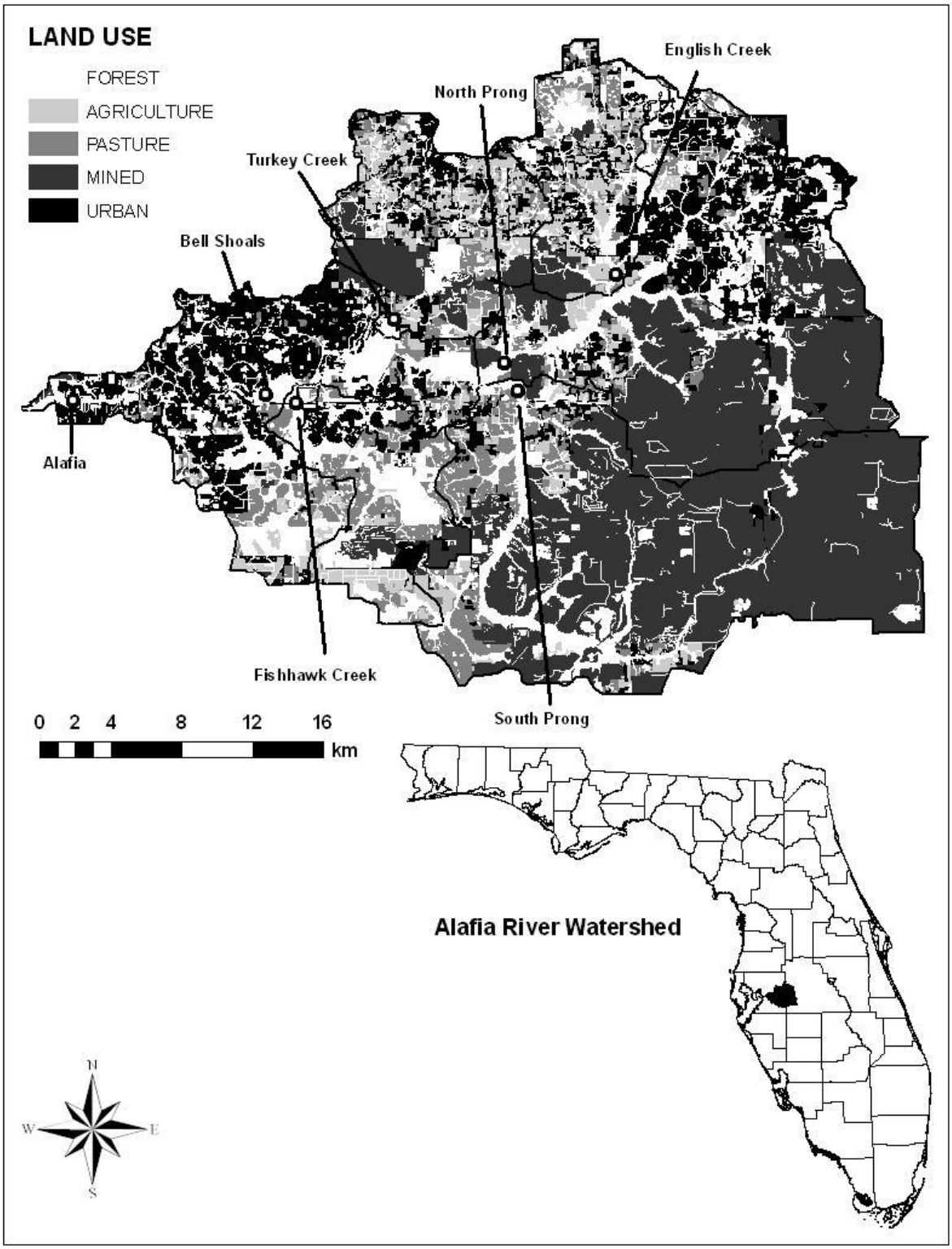

Figure 2-1. Location map and land uses in the various sub-basins of the Alafia River Watershed.

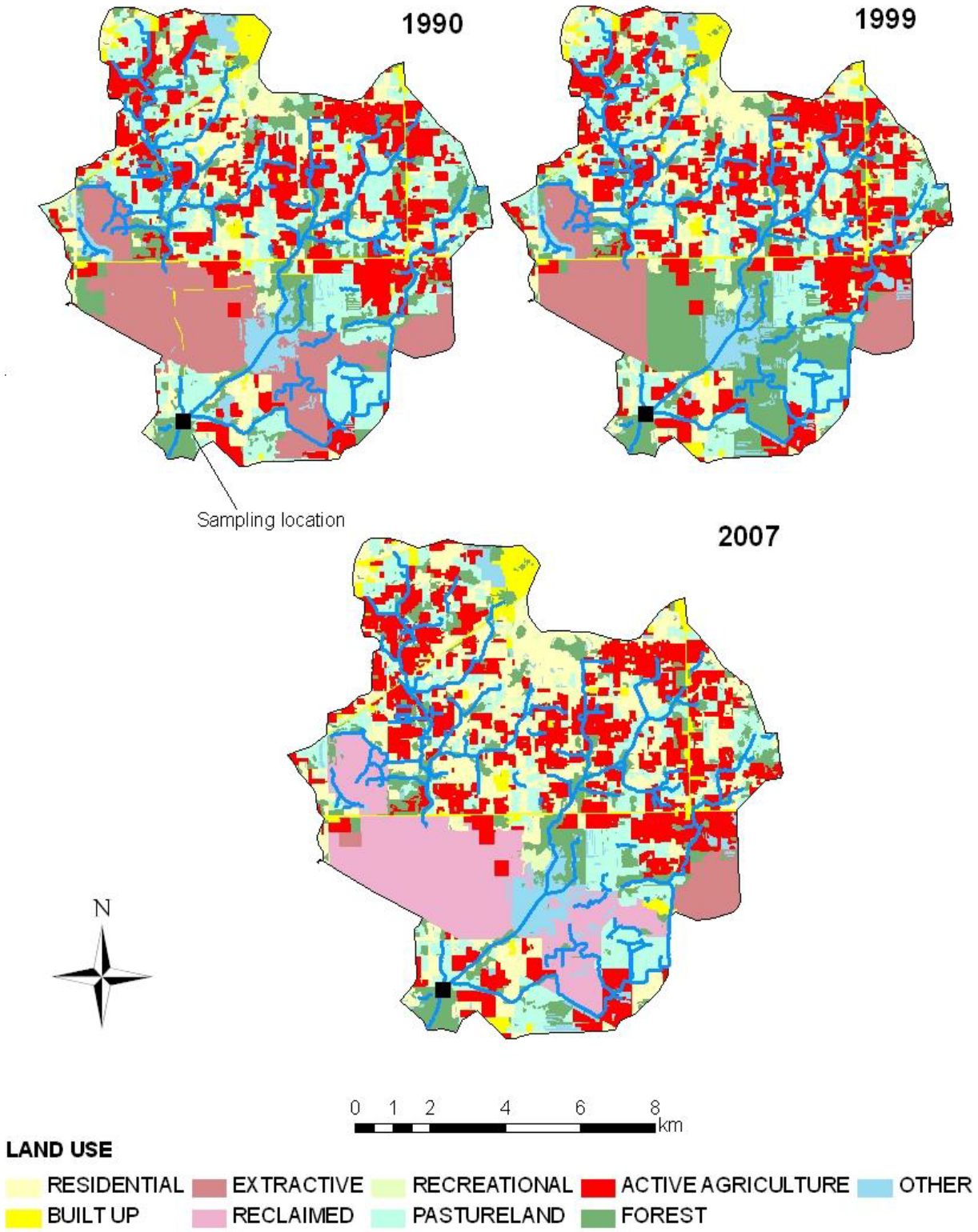

Figure 2-2. Land use in the Turkey Creek sub-basin in 1990, 1999, and 2007.

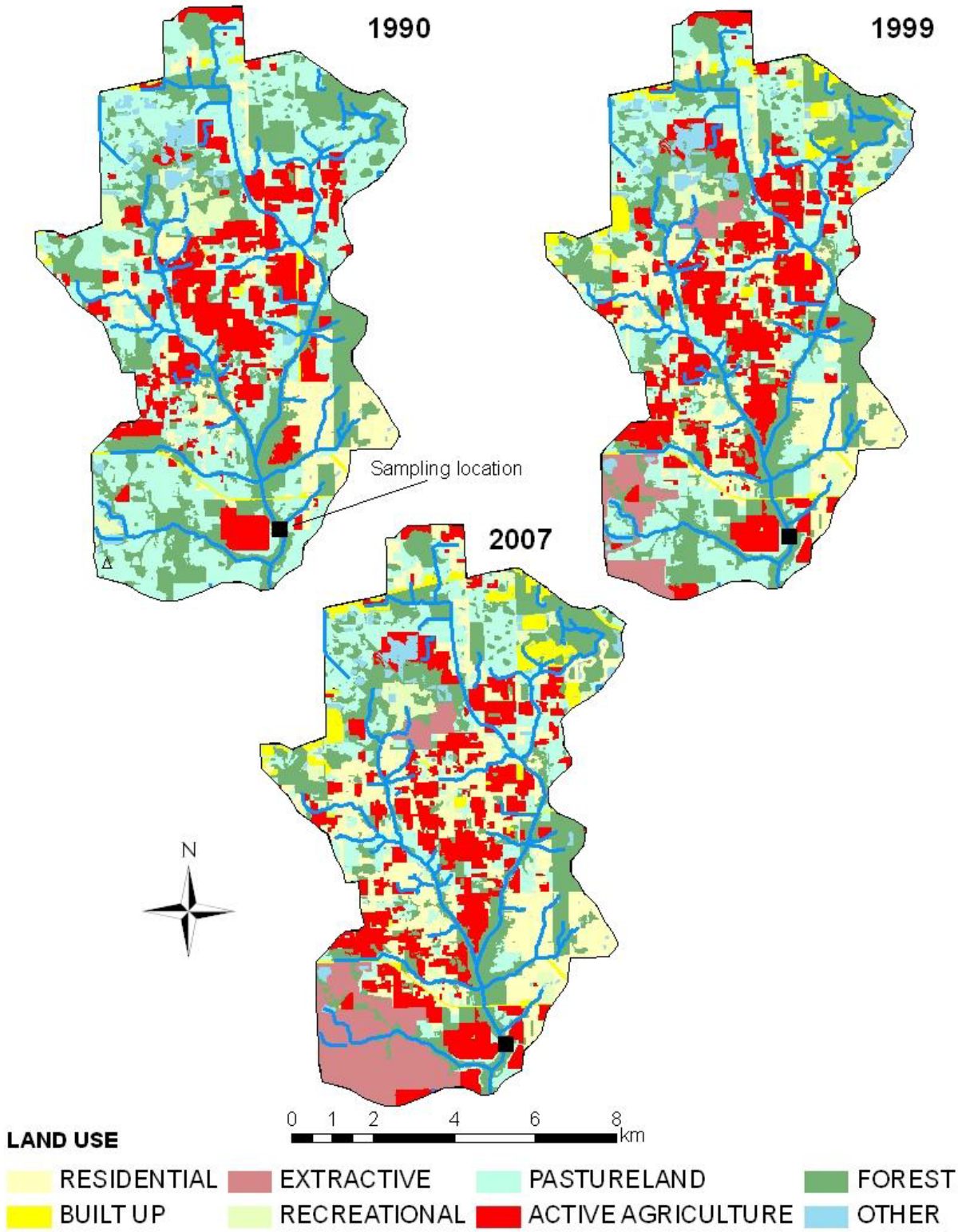

Figure 2-3. Land use in the English Creek sub-basin in 1990, 1999, and 2007.

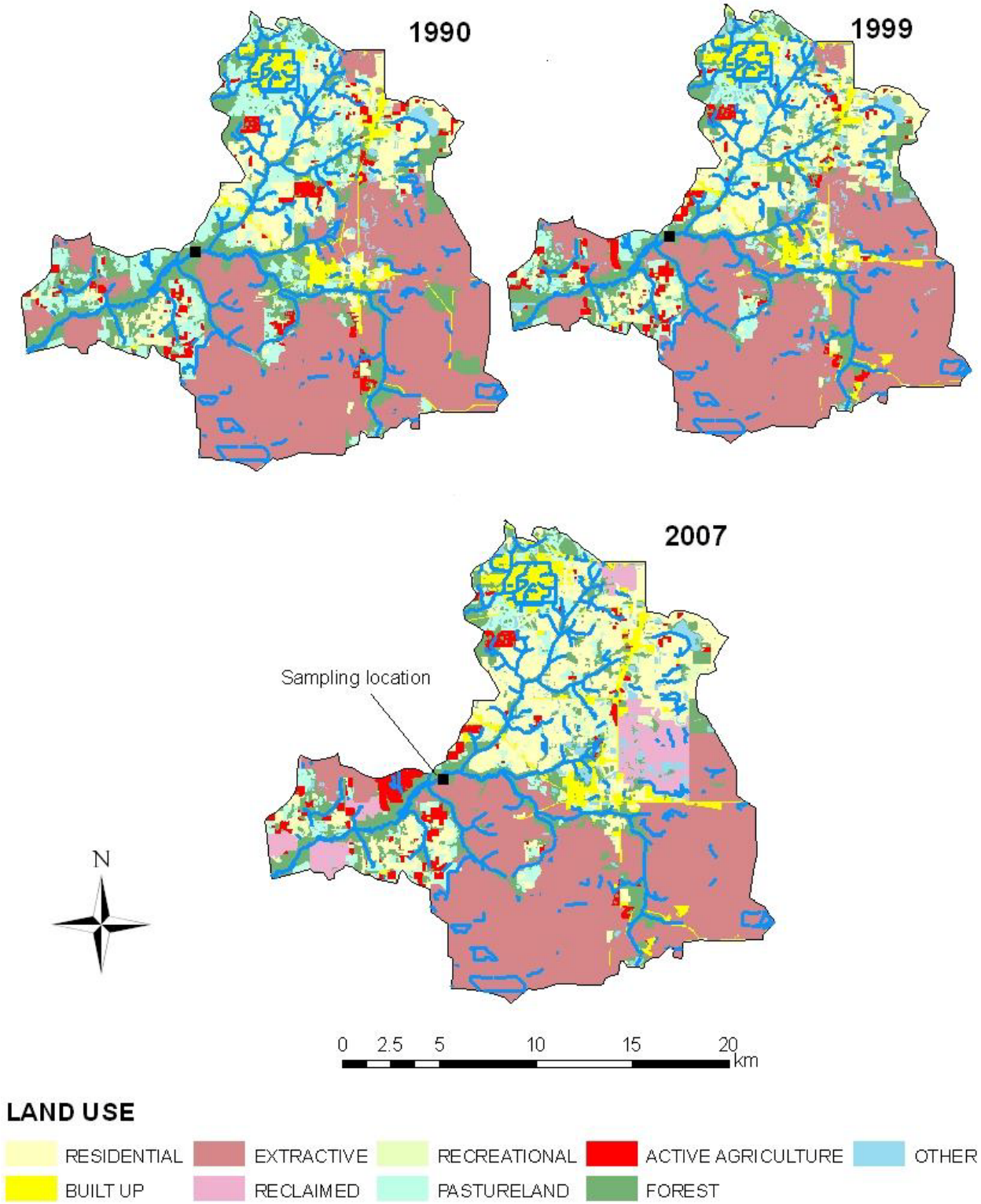

Figure 2-4. Land use in the North Prong sub-basin in 1990, 1999, and 2007.

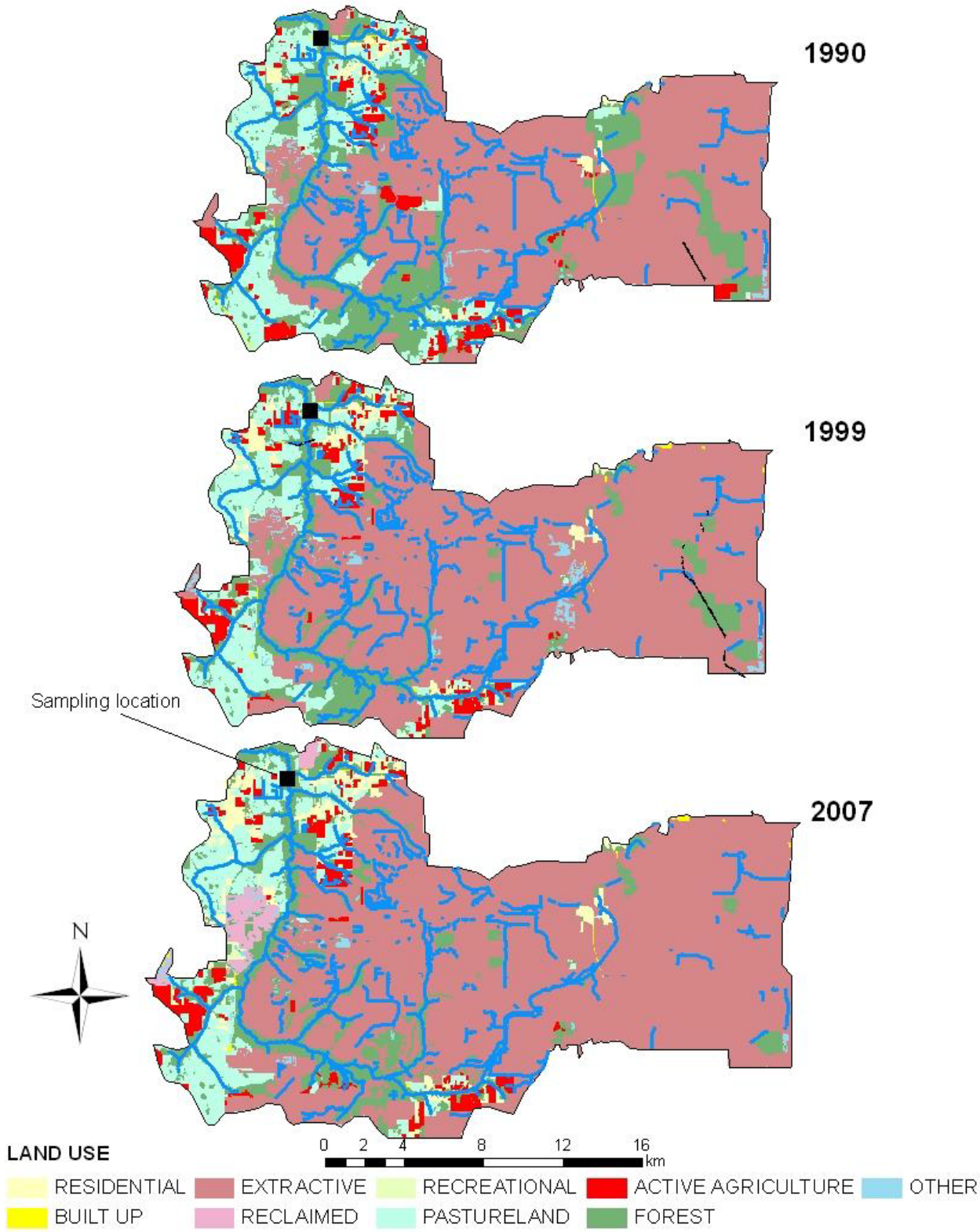

Figure 2-5. Land use in the South Prong sub-basin in 1990, 1999, and 2007.

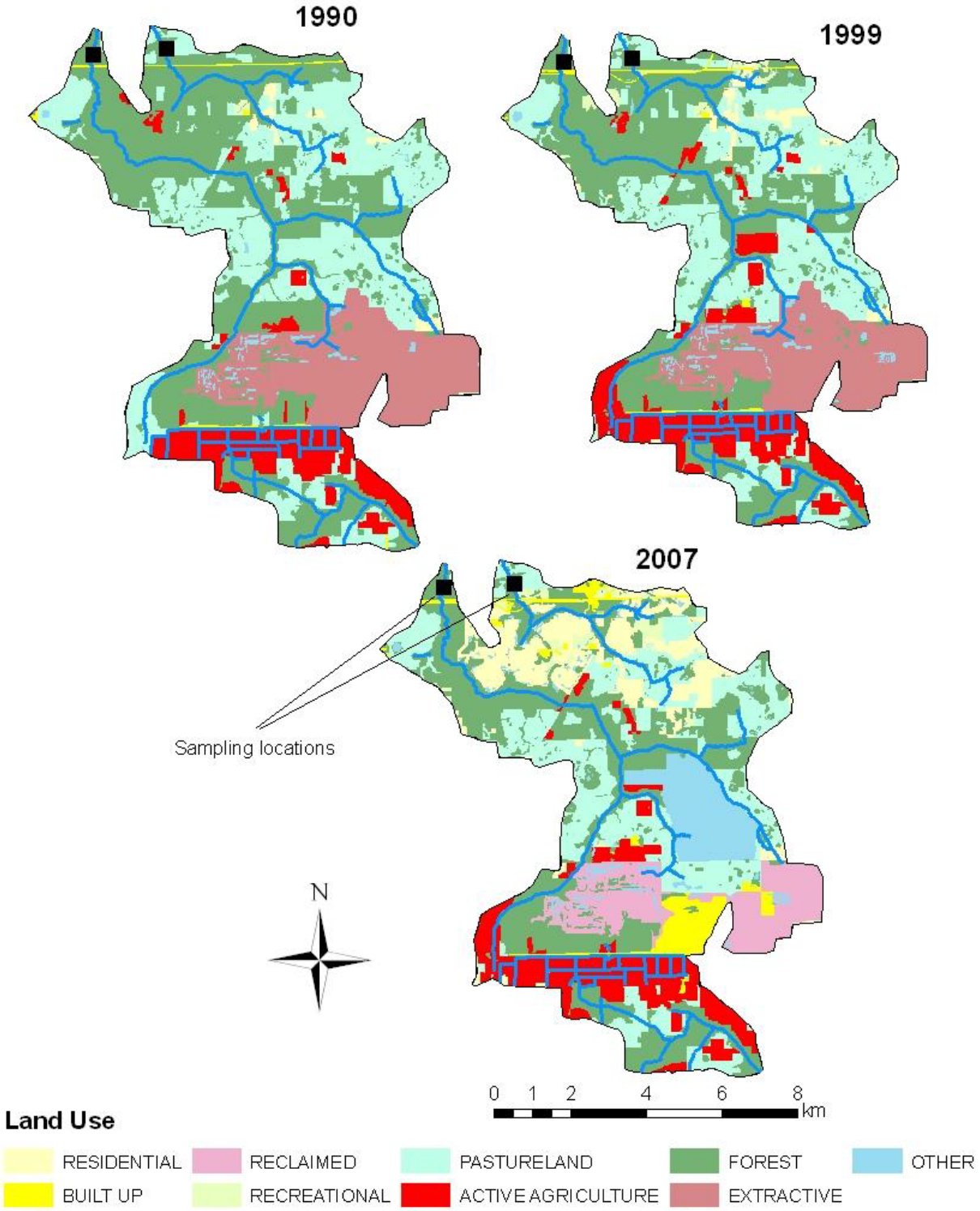

Figure 2-6. Land use in the Fishhawk Creek sub-basin in 1990, 1999, and 2007.

CHAPTER 3
NITROGEN TRANSPORT IN AN URBAN WATERSHED

Abstract

Eutrophication affects freshwater, estuarine, and marine ecosystems worldwide. Many nitrogen (N) limiting water bodies such as Tampa Bay estuary show accelerated eutrophication due to increase in nitrogen (N) concentrations. Understanding the processes and mechanisms controlling the N transport in a watershed are essential to devise strategies to prevent coastal eutrophication. In this study, we used 5 to 19 years of monthly stream-water concentrations data of inorganic and organic forms of N for seven sub-basins (19–350 km^2) of the Alafia River Watershed (total drainage area: 1085 km^2). Results showed that total N in stream waters ranged from 0.84 to 2.43 mg L^{-1}, was greater in the developed (23–35% urban land use) than undeveloped (3–14% urban land use) sub-basins. Total N was significantly ($P<0.05$) correlated with urban (r=0.83) but not with agricultural (r=0.49) land uses thereby indicating that the losses of N are greater from urban areas. Among N forms, organic N was dominant in undeveloped (66–71% of total N) than developed (30–44% total N) sub-basins while NO_3-N was dominant in developed (53–68% of total N) than undeveloped (25–30% of total N) sub-basins. Concentrations of NO_3-N were lower in wet season (June–September) compared with dry season (October– May) due to higher rainfall–runoff in wet season that may have caused dilution of NO_3-N. In contrast, greater concentration of organic N in wet season is possibly due to the greater transport of organic materials such as leaves and plant residues in high rainfall-runoff events that occurred during wet season. Trend analysis indicated that total N concentrations increased by 1.01% per year at the most downstream station during 1991–2009 and this increase was primarily due to the increased concentrations of organic N. Total N at two mainstem stations was 1.77–1.91 mg L^{-1}, which is close to the EPA proposed numeric total N of 1.79 mg L^{-1}.

Greater total N concentrations in three developed sub-basins (1.7–2.4 mg L^{-1}) suggest that targeting best management practices in these three urban sub-basins may be a resource efficient way to reduce N concentrations in this urban watershed.

Introduction

Nitrogen is a limiting nutrient for eutrophication in many coastal waterbodies in the US and elsewhere, including the Tampa Bay Estuary in Florida (USEPA, 2002; Dixon, 2009; TBEP, 2009). Major sources of N in water bodies are from point such as wastewater and industrial effluents and non-point such as runoff and leaching from urban and agricultural lands. Point source contributions have substantially reduced in the US following passage of Clean Water Act in early 1970 (Howarth et al., 2002). While non-point source N pollution is the major contributor of N loads in water bodies because of its diffuse nature (Diebel et al., 2009; Maxted et al., 2009). Major non-point sources in urban watersheds can be fertilized urban lawns, septic tanks, and pet waste (Brett et al., 2005; Rhodes et al., 2001). A logical approach to control non-point N pollution may be to develop an understanding of major N sources and hot spot areas in a watershed. This can be achieved by determining the N forms in streams that drain sub-basins with different land uses.

Different land uses in a watershed have been shown to receive different N inputs (Boyer et al., 2002; Kaushal et al., 2008). For example, in Northeastern watersheds of the US, Boyer et al. (2002) reported that the N inputs were positively correlated with the percentage of agricultural and urban land uses (r=+0.96) and negatively correlated with the forest land use (r =–0.77). Similarly, the net anthropogenic N inputs were six-times greater in agricultural (77 kg ha^{-1}) and two-times greater in suburban (25 kg ha^{-1}) than the forest (11.2 kg ha^{-1}) watersheds in Baltimore, US (Groffman et al., 2004). Losses of N in watersheds depend upon N inputs and therefore the anthropogenically influenced agricultural or urban watersheds result in greater N losses than

forested watersheds (Boyer et al., 2002; Han et al., 2009). Groffman et al. (2004) reported that total N was greater in streams draining agricultural (4–5 mg L^{-1}) and sub-urban (1–4 mg L^{-1}) as compared to the forested watersheds (< 0.25 mg L^{-1}). Similarly, concentrations of total N were greater in streams draining urban (1.5 mg L^{-1}) than forest (1.1 mg L^{-1}) watersheds in Seattle, US (Brett et al., 2005). Vidon et al. (2008) observed total N concentrations of 6.2–9.4 mg L^{-1} in intensively agricultural (corn–soybean) dominated watersheds in Indiana (Vidon et al., 2008). These and other studies have shown that total N concentrations are higher in streams that drain agricultural and urban watersheds as compared with forested watershed, primarily due to the greater inputs of N in the former than the later watersheds.

Land uses in a watershed also influence the forms of N lost (Scott et al., 2007). To understand the terrestrial N cycling and transport across spatial and temporal scales in watersheds with different land uses, understanding of different N forms in streams that drain different land uses is essential (Pellerin et al., 2006). Organic N (ON) forms have been shown to be the dominant forms in less developed watersheds such as forested or mixed cover than more developed watersheds such as intensive agriculture. Stanley and Maxted (2008) reported that ON was 68% (<0.3 mg L^{-1}) of total dissolved N (NO_3-N + NH_4-N + dissolved ON) in 84 Wisconsin streams. While in more anthropogenically influenced watersheds (urban and agricultural), inorganic N forms such as NO_3-N were dominant (Pellerin et al., 2006; Stanley and Maxted, 2008). For example, increased agriculture and urban land uses in the Mississippi River basin have been shown to double N concentration from 1.1 mg L^{-1} in 1902 to 2.2 mg L^{-1} in 1999 and most of this increase was in the NO_3-N, which increased from <55% (total N: 1.1 mg L^{-1}) in 1902 to >75% (total N: 2.2 mg L^{-1}) in 1999 (Goolsby and Battaglin, 2001; Turner and Rabalais, 2003). In a study on N budgets in 348 watersheds with varying land uses in North America,

Pellerin et al. (2006) reported that of the total dissolved N, ON was 35% in urban and 55% in forest streams. These studies provide evidence of land use specific controls on the fate and transport of different N forms.

Although the percent ON is lower in streams draining agricultural and urban land uses, the concentrations of ON may increase with anthropogenic activities. For example, Pellerin et al. (2006) observed that dissolved ON concentrations were 2–4 times greater in urban and agricultural than forest watersheds. In two watersheds dominated by pastures in Japan, Hayakawa et al. (2006) reported that urban land use of 0.2–4.3% was significantly correlated (r=+0.52) with dissolved ON. High concentrations of ON in anthropogenically influenced watersheds could be due to the inputs of organic N rich sources such as manures, composts, and other organic amendments in crops and urban lawns, contribution of organic N from onsite septic systems, and direct discharge of sewage effluents in streams (Kroeger et al., 2006; Scott et al., 2007). It is also plausible that NO_3-N in urban and agricultural watersheds is first taken up by microbes and vegetation, which on decomposition releases N in the ON forms, which can be subsequently transported to waters. Long-term N fertilization studies at the Harvard forest in Massachusetts have shown that dissolved ON concentrations in the forest floor increased as a result of elevated inorganic N deposition thereby representing the conversion of inorganic N to ON (McDowell et al., 2004). Wetlands and artificial retention ponds in many urban landscapes are common features, designed to reduce flooding events, which may stimulate additional reinforcing processes such as plant or microbial uptake and can denitrify NO_3-N resulting in reduced transport of NO_3-N (Groffman et al., 2004; Pellerin et al., 2004).

Another consequence of land use change primarily in urbanizing watersheds is the alteration of physical and hydrologic features that increase impervious area in the form of

rooftops, roadways, parking lots, sidewalks, and driveways (Carpenter et al., 1998; Tufford et al., 1998). The increased impervious area in urban watersheds leads to increased runoff due to altered and short flow paths compared to natural systems (Arnold and Gibbons, 1996; Lee and Heaney, 2003; Paul and Meyer, 2001). In addition, the loss of natural vegetation minimizes recycling and uptake of N due to reduced microbial and vegetative processes that immobilize N in the forest canopy, litter, soils, and organic matter (Abelho, 2001; Wahl et al., 1997). Together, increased flow and reduced vegetation decrease the residence time of water and N in the urban watersheds, which decreases N processing such as denitrification and thus make more N available for transport (Alexander et al., 2000; Green et al., 2004; Peterson et al., 2001). Therefore, the watersheds with greater development and modified hydrology are likely to export a higher amount of N to water bodies than less developed watersheds.

The Alafia River Watershed is an example of such a watershed, where land use has been continuously changing from natural areas to urban lands for the last 30+ years. As a result, several sub-basins of the watershed have modified hydrology–due to stormwater retention ponds and water convergence structures–to drain excess water during high flow events to avoid flooding. Two sub-basins of the watershed are dominant in mined land where phosphate mining is a commercial enterprise. We hypothesize that the 1) concentration of N forms may be different in sub-basins with diverse land uses and 2) the urbanization may increase the N concentrations in streams of the Alafia River Watershed. The objectives of this study were to (1) determine how different sub-basins (with different land uses) influence concentrations of different forms of N in stream waters; (2) investigate the influence of two distinct seasons (dry and wet) on concentrations of N forms in stream waters, and (3) evaluate the long term trends of N concentrations in different sub-basins.

Materials and Methods

Study Site Description

Refer to Chapter 2 for detailed description of sub-basins of the Alafia River Watershed.

Data Collection

Monthly concentrations data from 1991 to 2009 of total Kjeldahl N (TKN), NO_3-N, and NH_4-N were obtained from the Environmental Protection Commission of Hillsborough County (EPCHC) water quality database (http://www.epchc.org). Among the two mainstem stations, water quality data were available only for the Bell Shoals station for 19 years (1991–2009), while for the Alafia station the data were available for 9 years (1999–2009) (Table 3-1). Among other sub-basins in the watershed, 19 years of water quality data were available only for North Prong, South Prong, and Turkey Creek while the data availability for English Creek was from 1999 to 2009 and for Fishhawk Creek from 2005 to 2009.

Stream-water Collection and Analysis

Each month, a grab sample from surface water was collected from the channel thalweg (center of the stream flow) in plastic water bottles by EPCHC staff as per the surface water quality collection standard operating procedures. In brief, the water bottles were rinsed three times with the stream water before collection of the samples. The collected samples were chilled with ice and transported to the laboratory where samples were stored at 4 ^{o}C prior to analysis. Environmental Protection Commission Hillsborough County staff analyzed the surface water samples for TKN (EPA 350.2 method), NO_2-N+NO_3-N (SM 4500 NO_3), and NH_4-N (EPA 350.1) using a discrete analyzer. Other N fractions were calculated as follows: total N = NO_2-N+NO_3-N + TKN; organic N (ON) = TKN–NH_4.

Statistical Analysis

Mean, median, and standard deviations of N forms were calculated using MS Excel 2007. The GLIMMIX time series procedure in SAS Version 9.1 (SAS Institute, Cary, NC) was used to compare the N forms across different sub-basins as well as to determine the long term trends in N forms. The GLIMMIX procedure fits models to data with correlations or non constant variability and assumes normal random effects (SAS Institute, 2008). In this time series analysis, two kinds of effects were used: (1) fixed effects which included stream station and season of the year and (2) random effects which was the date of sample collection (monthly intervals). For first fixed effect (stream station), each station was treated as a group and the variance was pooled over the sites. Similarly for the second fixed effect (season), each wet (June–September) and dry (October–May) season at each station was treated as one group of observations. The date of sample collection from 1991–2009 for the each station was considered as random effect and therefore a time series was constructed. With this, we compared (1) the difference in N forms at each of the station averaged over all sampling dates and (2) differences in pooled mean concentrations of N forms during wet and dry seasons at each station using $P \leq 0.05$ as significance level. In addition, same time series with fixed and random effects were used to determine the trends in N forms over the period of study. The concentrations of different forms of N were logarithmically transformed to equalize variances and normalize skewed data and were back transformed to present means of N forms in more relevant manner.

Various statistical techniques have been used to determine the long term water quality trends (Goodrich et al., 2009; Johnson et al., 2009; Richards et al., 2008). Most common methods include non parametric Mann-Kendall and Seasonal Kendall for determination of long term trends in water quality (Daroub et al., 2009; Johnson et al., 2009). Only a few studies have used GLIMMIX procedure (e.g., Goodrich et al., 2009) and no studies have attempted to use a

mix of more than one statistical procedure. Therefore, in addition to GLIMMIX procedure, we determined the long term trends using Seasonal Kendall procedure. In Seasonal Kendall, trend is calculated by comparing all potential data pairs. If the later value in the pair (in time) is higher than the first, a plus sign is scored. If the later value in the pair is lower than the first, a minus sign is scored. If the results find an equal number of pluses and minuses, then there is no discernible trend. In other words, there is just as much of a likelihood that a pair of data values will be higher (or lower) than the next one. If the results show more pluses than minuses, this would indicate that a positive trend is likely (Hirsch et al., 1982).

The trend in both GLIMMIX and Seasonal Kendall procedures is defined by the rate of change in the concentration of a constituent over time, which is referred to as the trend slope. The trend slope can be expressed either as change in original units per year [S (0)], or as a percent of the mean concentration of water quality variable [S (%)]. The former is the median slope of all pair wise comparisons (each pair wise difference is divided by the number of years separating the pair of observations) while the latter is produced by dividing the slope (in original units per year) by the mean and multiplying by 100.

The N forms concentrations data were divided into two time periods: 1991–2000 and 2001–2009. To determine the effect of land use change on N forms in corresponding sub-basins, the land use data of 1999 and 2007 was correlated with N concentrations data of 1991–2000 and 2001–2009, respectively using SAS PROC CORR procedure.

Results

Chemical Characteristics of Stream Waters

During 1991–2009, mean monthly temperature in stream waters was 22–23 ^{o}C (Fig. 3-2). The concentration of DO in stream waters was lowest at Alafia (3.1 mg L^{-1}) than Bell Shoals (6.4 mg L^{-1}) and other sub-basins (5.3–7.3 mg L^{-1}) of the Alafia River Watershed. Among the sub-

basins, the DO concentration was significantly ($P < 0.05$) lower at one developed (English Creek; 5.3 mg L^{-1}) than other sub-basins. Mean pH of the stream waters was similar (7.2–7.5) at all the stations of the Alafia River Watershed (Fig. 3-2). In contrast to pH, the mean EC of the stream waters was atleast one order of magnitude greater at one mainstem station near to the Tampa Bay (Alafia; 7548 µS cm^{-1}) than Bell Shoals (443 µS cm^{-1}) and other sub-basins (214–556 µS cm^{-1}). Among the sub-basins, EC was significantly lower at one undeveloped sub-basin (Fishhawk Creek: 214 µS cm^{-1}) than other developed and undeveloped sub-basins.

Concentrations of Nitrogen Forms in Streams Draining Different Sub-basins

During 1991–1999, mean monthly total N concentration at the mainstem station (Bell Shoals) that drains 89% of the watershed was 1.65 mg L^{-1} (Fig. 3-3A). Total N was significantly ($P < 0.05$) greater at two developed (1.45–1.74 mg L^{-1}) than one undeveloped sub-basin (1.06 mg L^{-1}). Among the two developed sub-basins, Turkey Creek had significantly ($P < 0.05$) greater total N than North Prong.

Total N concentrations were greater during 2000–2009 than 1991–1999 at one mainstem (Bell Shoals), two developed (North Prong and Turkey Creek), and one undeveloped (South Prong) sub-basins of the Alafia River Watershed (Fig. 3-3A). Mean monthly total N at two mainstem stations (Alafia and Bell Shoals; urban land use 19–20%) was 1.77–1.91 mg L^{-1} (Fig. 3-3A). Total N concentrations in stream waters were significantly ($P<0.05$) greater in all the developed sub-basins (English Creek, Turkey Creek, and North Prong; 1.67–2.43 mg L^{-1}) than undeveloped sub-basins (South Prong and Fishhawk Creek; 0.84–1.21 mg L^{-1}). Differences in total N concentrations in streams among developed and undeveloped sub-basins were observed. For example, among the developed sub-basins, English Creek had significantly greater total N (2.43 mg L^{-1}) than Turkey Creek (1.96 mg L^{-1}) and North Prong (1.67 mg L^{-1}). Similarly in the

undeveloped sub-basins, total N was significantly higher in South Prong (1.21 mg L^{-1}) as compared to Fishhawk Creek (0.84 mg L^{-1}).

During 1991–1999, mean monthly ON concentration at the mainstem station (Bell Shoals) was 0.49 mg L^{-1} (30% of total N) (Fig. 3-3B). The ON concentration in the stream waters was similar in all the sub-basins (0.57–0.63 mg L^{-1}). In contrast to the concentrations, the percent of ON was greater in undeveloped (53% of total N) than two developed (36–41% of total N) sub-basins.

Concentrations of ON were greater during 2000–2009 than 1991–1999 in streams draining mainstem, two developed, and one undeveloped sub-basins. Among the mainstem stations, mean monthly concentration of ON was significantly ($P < 0.05$) greater at the most downstream Alafia (1.02 mg L^{-1}; 58% of total N) as compared to next upstream Bell Shoals (0.75 mg L^{-1}; 39% of total N) (Fig.3-3B). All the developed and undeveloped sub-basins had a narrow range of stream ON (0.73–0.77 mg L^{-1}) except for a significant lower concentration at Fishhawk Creek (0.60 mg L^{-1}). However, the percent of ON was much greater in streams draining undeveloped (66–71% of total N) than developed (30–44% of total N) sub-basins.

At the mainstem station (Bell Shoals), the NO_3-N was the dominant N form (1.13 mg L^{-1}; 69% of total N) during 1991–1999 (Fig. 3-3C). In contrast to ON, NO_3-N concentrations were two folds greater in two developed (0.82–1.07 mg L^{-1}; 57–62% of total N) than one undeveloped sub-basin (0.47 mg L^{-1}; 45% of total N). Among the two developed sub-basins, Turkey Creek had significantly ($P < 0.05$) greater NO_3-N than North Prong.

The concentrations of NO_3-N were similar during 1991–1999 and 2000–2009 in all the streams draining different sub-basins (Fig. 3-3C). Concentrations of NO_3-N at Bell shoals were significantly ($P < 0.05$) greater (1.14 mg L^{-1}; 60% of total N) than the most downstream Alafia

(0.67 mg L^{-1}; 38% of total N). Among the sub-basins, NO_3-N followed the total N pattern and was significantly greater in developed (0.89–1.66 mg L^{-1}; 53–68% of total N) than undeveloped (0.21–0.37 mg L^{-1}; 25–30% of total N) sub-basins.

At all study stations, mean monthly concentrations of NH_4-N were much lower (<0.1 mg L^{-1}; 2–5% of total N) than both ON and NO_3-N during 1991–1999 and 2000–2009 (Fig. 3-3D).

Seasonal Variations in Chemical Characteristics in Stream Waters Draining Different Sub-basins

At two mainstem stations (Alafia and Bell Shoals), the mean temperature of the stream waters was significantly (P< 0.05) greater in wet (26–27 ^{o}C) than dry season (20–21 ^{o}C) (Fig. 3-4). A similar increase in temperature of stream waters in wet (26–27 ^{o}C) than dry (18–20 ^{o}C) seasons was found in developed and undeveloped sub-basins. The seasonal variation showed opposite trends in DO concentrations than temperature of the stream waters possibly due to greater biological activity in stream waters with greater temperature. For example, at two mainstem stations, the DO concentration of the stream waters was greater in dry (3.4–6.8 mg L^{-1}) than wet season (2.7–5.9 mg L^{-1}). Among the sub-basins, the concentration of DO in stream waters was 5.6–8.1 mg L^{-1} in dry season and decreased to 4.6–6.1 mg L^{-1} in wet season (Fig. 3-4). This decrease in DO concentration of the stream waters was significant (P< 0.05) in all the sub-basins except for English Creek.

At two mainstem stations, the pH of stream waters was greater but not significantly (P< 0.05) in dry than wet seasons (Fig. 3-4). Among sub-basins, the pH of the stream waters was greater in dry season (7.4–7.6) and decreased in wet season (6.9–7.3); however the decrease was significant (P<0.05) only at Fishhawk Creek. Similarly, the EC of the stream waters was greater but not significantly (P<0.05) different in dry than wet season in all study basins.

Seasonal Variations in Concentrations of Nitrogen Forms in Streams Draining Different Sub-basins

At two mainstem stations (Alafia and Bell Shoals), the mean total N was slightly higher, but not significant ($P < 0.05$), in dry (1.83–1.84 mg L^{-1}) than wet (1.61–1.69 mg L^{-1}) season (Fig. 3-5A). All the developed sub-basins (Turkey Creek, English Creek, and North Prong) had greater total N in dry than wet season while the undeveloped sub-basins had greater total N in wet than dry season (Fig. 3-5A). However, the seasonal variation was significant ($P < 0.05$) only in Fishhawk Creek and English Creek.

Mean ON concentrations were lower in dry season and increased in wet season at all sites (Fig. 3-5B; Fig. 3-6). The magnitude of this increase was greater at Bell Shoals (from 0.52 to 0.82 mg L^{-1}) as compared to Alafia (from 0.99 to 1.03 mg L^{-1}). Among the developed sub-basins, the increase in ON concentration during wet season was greatest at English Creek (from 0.57 to 1.03 mg L^{-1}) than Turkey Creek and North Prong (from 0.60–0.64 to 0.80–0.83 mg L^{-1}). In undeveloped sub-basins, ON was 0.48–0.58 mg L^{-1} in dry season which increased to 0.83–0.88 mg L^{-1} in wet season.

In contrast, NO_3-N was lower in wet than dry season at all sites (Fig. 3-5C; Fig. 3-6). For example, at two mainstem stations, NO_3-N in dry season was 0.75–1.30 mg L^{-1}, which decreased to 0.51–0.84 mg L^{-1} in the wet season. Similarly, among developed sub-basins, the decrease in NO_3-N in wet season compared to dry season was significant at English Creek (from 2.07 to 0.91 mg L^{-1}) but not at Turkey Creek (from 1.24 to 0.85 mg L^{-1}) and North Prong (from 0.98 to 0.65 mg L^{-1}). In undeveloped sub-basins, the decrease in NO_3-N was significant only at Fishhawk Creek (from 0.23 to 0.17 mg L^{-1}).

Concentrations of NH_4-N were not significantly different among dry and wet seasons at all study stations (Fig. 3-5D; Fig. 3-6). But, NH_4-N was greater at the most downstream station (Alafia) than other sites in both wet and dry seasons.

Long Term Trends in Flow Un-weighted Nitrogen Forms in Streams Draining Different Sub-basins

Total Nitrogen

The longest data record (19 years) was only available for one mainstem station (Bell Shoals) that drains 89% of the watershed, two developed (Turkey Creek and North Prong), and one undeveloped (South Prong) sub-basin (Table 3-7). According to Seasonal Kendall trend analysis, none of the total N concentrations trends were significant (P< 0.05) for these four sub-basins during the study period. However, the concentrations of total N were increasing at Bell Shoals (+0.17% per year; 2.79 µg L^{-1} per year) (Fig. 3-7). Among the sub-basins, total N showed an increasing trend +1.7% or 18.9 µg L^{-1} per year at South Prong and +1.5% or 29.1 µg L^{-1} per year at Turkey Creek and a decreasing trend at North Prong (–0.42% or 6.7 µg L^{-1} per year). Among the stations with 10 years of data record, the mainstem station Alafia and developed English Creek showed decreasing but not significant (P< 0.05) total N trends.

The total N concentration trends estimated with the GLIMMIX procedure were similar to Seasonal Kendall but the magnitude of trend slopes was variable. The GLIMMIX model showed a significant (P<0.09) overall increasing total N trend of +1.01% per year at the mainstem Bell Shoals station which equates to approximately 20% increase (0.33 mg L^{-1}) in the total N over 19-years (Fig. 3-7). Total N significantly increased at Turkey Creek (+1.02% per year; P< 0.005) and South Prong (+1.07% per year; P< 0.03) but not at North Prong (–1.11% per year; P< 0.64) during 1991–2009. The study stations with 10 years of data record (Alafia and English Creek) showed decreasing but not significant (P< 0.05) total N concentration trends.

Organic Nitrogen

Seasonal Kendall trend analysis showed that the ON concentrations were increasing at all the four study stations with 19-years of data record (Fig. 3-8). At Bell Shoals, total N showed an increasing but not significant (P< 0.45) trend (+1.8% per year) which equates to 35% increase in mean ON concentration during 1991–2009. The increasing ON trends were significant (P< 0.001) at Turkey Creek (+2.5% per year) but not at North Prong (+0.72% per year; P< 0.46) and South Prong (+1.95% per year; P< 0.25). None of the trends were significant in two sub-basins with 10 years of data record.

The GLIMMIX procedure showed increasing ON concentration trends at four sub-basins with 19 years of data record (Fig. 3-8). Overall, at Bell Shoals the ON concentration trend was (+0.94% per year; P= 0.001) which equates to approximately 19% increase in ON concentration over 19-years. Among the sub-basins, the ON concentrations significantly (P< 0.001) increased at Turkey Creek (+0.94% per year), South Prong (+0.95% per year) but not at North Prong (+1.00% per year). During 1999-2009, Alafia station showed decreasing (–2.45% per year) as compared to increasing trends at English Creek (+0.65% per year).

Nitrate Nitrogen

As per Seasonal Kendall trend analysis, none of the NO_3-N concentrations trends were significant (P< 0.05), however, the NO_3-N decreased at Bell Shoals (–0.27% per year) during 1991–2009 (Fig. 3-9). Among the sub-basins, the NO_3-N concentration trend was decreasing at North Prong (–0.1% per year) and South Prong (–2.7% per year) but not at Turkey Creek (+0.18% per year) during 1991–2009. During 1999–2009, Alafia station showed an increasing NO_3-N concentration trend (+5.4% per year).

Using GLIMMIX procedure, none of the NO_3-N concentrations trend was significant (P< 0.05); however the overall trend at Bell Shoals was decreasing (–1.04% per year) during 1991–

2009 (Fig. 3-9). Turkey Creek showed an increasing NO_3-N concentration trend (+1.13% per year) in contrast to decreasing trends at North Prong (–0.31% per year) and South Prong (–0.98% per year). During 1999–2009, the NO_3-N concentration trends were not significant at Alafia (+0.96% per year) and English Creek (–1.74% per year).

Ammonium Nitrogen

Both the Seasonal Kendall trend analysis and GLIMMIX procedure showed non-significant trends NH_4-N at all the sub-basins of the Alafia River Watershed (Fig. 3-10). The concentrations of NH_4-N remained lower (<0.4 mg L^{-1}) during the study period at all the sub-basins.

Long Term Trends in Flow Weighted Nitrogen Forms in Streams Draining at Mainstem Station

At the mainstem station that drains 89% of the Alafia River Watershed showed increasing but not significant (P< 0.241) total N concentration trends during 1991–2009 (Table 3-2). Mean concentrations of total N were greater during 2000–2009 (1.82 mg L^{-1}) than 1991–1999 (1.53 mg L^{-1}) reflecting the increasing GLIMMIX trends in terms of actual increase in concentrations. The ON concentrations showed significant (P< 0.01) increasing trends of +1.05% per year (+7.0 µg L^{-1} per year; 0. 14 mg L^{-1} in 19 years). Similar to total N, mean ON was greater during 2000–2009 (0.81 mg L^{-1}) than 1991–1999 (0.55 mg L^{-1}). In contrast to ON, flow weighted NO_3-N concentration trends were not significantly (P< 0.487) different for 1991–1999 (0.94 mg L^{-1}) and 2000–2009 (0.97 mg L^{-1}).

Long Term Trends in Nitrogen Loads at Mainstem Station

At mainstem station (Bell Shoals), total N loads were not significant in wet and dry seasons during 1991-2009 (Table 3-2). The non significant trends in the N loads during wet and

dry seasons could be due to greater variations in N loads and reduced number of data points in wet and dry seasons.

Relationship between Land Use and Nitrogen Forms

Total N concentrations were significantly ($P<0.05$) correlated with the percent urban (residential + built up) land use (r=+0.83) in the watershed (Fig. 3-11). This positive correlation was probably due to the influence of urban land use on NO_3-N (r=+0.78; $P<0.05$) rather than ON (r=+0.28) concentrations during the study period. The percent agricultural land use was positively but not significantly ($P<0.05$) correlated with total N (r= +0.49) and NO_3-N (r= +0.53). The pasture and forest land uses were not significantly correlated with any of the N forms (r= <0.30).

Discussion

Influence of Land Uses on Total Nitrogen Concentrations in Stream Waters

Mean monthly concentrations of total N at two mainstem stations (1.7–1.9 mg L^{-1}) approached the EPA's proposed numeric total N value of 1.79 mg L^{-1} for the region (EPA, 2010). These total N concentrations were greater than reported for Hillsborough County lakes value of 1.12 mg L^{-1} (Florida Lakewatch Program, 2005). However, total N was much lower than corn-soybean dominated watersheds (6.2–9.4 mg L^{-1}) in Indiana, US (Vidon et al., 2008). Lower total N concentrations in the Alafia River Watershed may be to the low agricultural land use (8%) while watersheds in Indiana had more than 60% of row crops land use. In our study, total N concentrations were similar to values reported for the urban and forest watersheds (1.1–1.5 mg L^{-1}) in Seattle, US (Brett et al., 2005).

The three developed sub-basins (23–35% urban land use) had greater total N (1.67–2.43 mg L^{-1}) than undeveloped sub-basins (3–14% urban land use) (0.84–1.21 mg L^{-1}). Total N concentrations were significantly ($P< 0.05$) positively correlated with urban land use (r= +0.83)

(Fig. 3-11). While total N was positively but not significantly ($P < 0.05$) correlated with agricultural (r=+0.49) and no relationship was observed between total N and forest and pasture land uses (r= <0.30). This indicates that the N concentrations significantly increase with urbanization of the watershed. The strong correlation between percent urban land use and NO_3-N concentrations (r=+0.78) may be due to the runoff of fertilizers containing N from urban/residential lawns. Overall, greater concentrations of total N in urban than forest and pasture land uses may be due to the higher N inputs in the former than later land uses (Boyer et al., 2002; Groffman et al., 2004). Furthermore, in urban lands impervious areas result in greater transport of N (Alexander et al., 2000; Green et al., 2004; Peterson et al., 2001) resulting in higher total N concentrations in developed than undeveloped sub-basin streams.

Among the three developed sub-basins, the total N concentrations were significantly ($P<0.05$) different during 2000–2009. Greater total N concentrations at English Creek than Turkey Creek and North Prong could be due to the greater urban land use (35%) in English Creek than North Prong and Turkey Creek (23–24%). A wastewater treatment plant discharges 0.11 m^3 sec^{-1} wastewater with total N concentration of 2.76 mg L^{-1} into the English Creek (SWFWMD, 2007). The total N concentrations in developed sub-basin vary inversely with size of the sub-basin. The length of the streams increases with the size of the sub-basin, which provides opportunities for the N removal processes such as denitrification in riparian buffer zones as well as within the stream resulting in lower concentrations of N (Alexander et al., 2000; Seitzinger et al., 2002; Alexander et al., 2009). These factors might have resulted in significant differences in N concentrations in three developed sub-basins. On the other hand, lower total N concentration in Fishhawk Creek that had 14% urban land (0.84 mg L^{-1}) than South Prong that had 3% urban land (1.21 mg L^{-1}) could be because of greater land area in forest in the former

(32%) than later (15%) sub-basin (Table 3-1). This highlights the importance of other land uses such as forest in addition to urban and agricultural land use in modifying the net total N losses in sub-basins.

Land Uses and Forms of Nitrogen Concentrations in Stream Waters

In our study, NO_3-N was 25–30% of total N in undeveloped and 53–68% of total N in developed sub-basins. The percent urban land use was strongly correlated with NO_3-N concentrations (r=+0.78) but not with ON concentrations (r=+0.28). This suggested that the increase in total N concentrations in urban land uses is primarily driven by NO_3-N probably due to the runoff losses of the N fertilizers applied to the urban lawns. Similarly, Stanley and Maxted (2008) in 84 streams in Wisconsin reported that NO_3-N was 75% of total dissolved N in urban compared to 30% in the forested streams. In a review on 348 watersheds across North America, Pellerin et al. (2006), reported that NO_3-N was 65% of total N in urban (>50% urban land use) and 35% of total N in forest (>90% forest land use) watersheds.

In contrast to decreasing percentages of ON in developed sub-basins, the concentrations of ON remained similar in developed (0.73–0.77 mg L^{-1}) and undeveloped sub-basins (0.60–0.79 mg L^{-1}). This indicates the existence of enough ON sources in urban areas such as contributions from septic tanks, grass cuttings of urban lawns, and deciduous leaves fallen on the ground (Kroeger et al., 2006; Scott et al., 2007). In addition, more impervious areas in urban areas may increase the runoff resulting in greater transport of these organic materials that contain ON (Carpenter et al., 1998; Tufford et al., 1998). Recent studies suggest that microbial transformations of NO_3-N to ON may act as an important source of ON in urban watersheds (McDowell et al., 2004; Pellerin et al., 2006). In our study, urban land use was slightly positively correlated (r=+0.28) with ON concentrations. Florida has a warm climate where the existence of wetlands and artificial stormwater retention ponds might play a stimulating role for biotic

conversion of NO_3-N into ON resulting in greater concentrations of ON in streams draining urban land uses (Groffman et al., 2004; Pellerin et al., 2004). Similarly, greater proportion of ON was found at the most downstream Alafia stations (58% of total N) than Bell Shoals (39% of total N) (Fig. 3-6). Alafia station is close to the Tampa Bay estuary where the velocity of the water decreases and thus this may provide more favorable conditions for denitrification and/or conversion of NO_3-N to ON via vegetation/microbial uptake (Groffman et al., 2004).

Seasonal Impacts on Nitrogen Forms in Stream Waters

The NO_3-N concentrations in stream waters were greater in dry season and decreased in wet season in all the sub-basins (Fig. 3-5). This can be explained by the significantly ($P<0.05$) greater temperature in wet season that might increase the biological uptake and denitrification of NO_3-N resulting in lower losses of NO_3-N in wet than dry season (Alexander et al., 2009; Chen and Driscoll, 2009). Due to greater biological activities in the stream waters, the concentration of DO is lower in wet than dry season in all the streams (Fig. 3-4). This provides an indication of greater denitrification losses of NO_3-N resulting in lower concentrations of NO_3-N in wet than dry season. Another probable reason for decreased NO_3-N concentrations in wet season could be the shift in flow-paths from groundwater to stormwater in wet season. In the Alafia River Watershed, EC of stream water is lower in wet than dry season thereby representing the dilution of the stream waters with stormwater runoff during the wet season. Similar to other salts (EC), NO_3-N concentrations decrease with greater stormwater runoff in wet season. This dilution of NO_3-N concentration in the stream waters during the wet season contradicts previous studies, who reported higher concentrations (flushing) of NO_3-N with greater runoff in wet season (Chen and Driscoll, 2009; Green et al., 2004; Qian et al., 2007; Royer et al., 2006). In general, the flushing of the NO_3-N with stormwater in wet season usually occurs when excess of NO_3-N is present in the watershed soils and other sources. For example, in the Indian River Lagoon,

Florida, fertilizers are applied to citrus crop during the wet season and the excess of NO_3-N is flushed with rain resulting in greater concentrations of NO_3-N in wet than dry season (Qian et al., 2007). Similarly, the watersheds in Midwest, US, are row crops dominated which receive greater N inputs and therefore the NO_3-N concentrations increase with greater drainage from the watersheds (Vidon et al., 2008). The Alafia River Watershed is not as intensively cultivated as the watersheds of the US Midwest and the Indian River Lagoon, therefore greater water is available due to modified urban drainage for dilution of the dissolved forms of N (NO_3-N) resulting in decreased concentration of NO_3-N during wet than dry season.

In contrast to NO_3-N, transport of particulate forms of N which represents ON is greater with greater storm water runoff in wet than dry season (data not shown). The particulate N forms could be decomposing products of leaf litter, grass cuttings of lawns, and soil sediments (Culbert and France, 1995). Therefore, concentrations of ON were greater in wet season than dry season in the Alafia River Watershed.

Long Term Trends in Nitrogen Concentrations

In our study, the Seasonal Kendall and GLIMMIX procedures showed similar trends (increasing or decreasing), though the magnitude of the trend slopes differed by 0 to 14% per year among two procedures (Fig. 3-7, 3-8, 3-9, 3-10). These differences in trend slopes appear to be associated with the conceptual difference in the procedures of two methods. For example, Seasonal Kendall trend analysis compares the change in concentrations of nutrients with time (slope) for each point and the median slope is calculated as a summary statistic describing the magnitude of the trend (Johnson et al., 2009; Qian et al., 2007). On the other hand, GLIMMIX procedure fits the linear lines through the data and slope is the rate of change in concentration with time at any of two points (SAS, 2008). Therefore, the differences in the magnitude of slopes appear in the trend analysis in two methods. In general, Seasonal Kendall trend analysis

determines the trends at a single location. However, GLIMMIX procedure can be used to compare the mean concentrations at multiple locations as well as has the ability to include many parameters such as stream discharge, seasonal variation, distance of the mainstem, and location of the station etc (Goodrich et al., 2009). In this study, GLIMMIX procedure has shown the significant variations in mean and seasonal variations in N concentrations at different stations.

The causes for the concentration trends can be either 1) natural such as the changes in precipitation and evapotranspiration resulting in variations in flow, or 2) anthropogenic such as changes in land use, nutrient management practices in the watersheds. The flow weighted and flow un-weighted concentration trends can help discriminate the effects of natural and anthropogenic changes on nutrient concentrations in streams. In the analysis of trends in flow weighted concentrations, the effects of natural changes in stream flow on concentration are removed and therefore flow adjustment of nutrient concentrations allows trends due to anthropogenic changes to be assessed. In the analysis of trends in observed flow un-weighted concentrations, no adjustments are made for any natural or anthropogenic influence. Therefore, the net effects of all simultaneous influences on concentration are evaluated, allowing for the assessment of nutrient concentrations in streams relative to water quality standards of Environmental Protection Agency and the condition of aquatic communities (Sprague and Lorenz, 2009).

At Bell Shoals that drains 89% of the watershed, increasing trends were found in flow un-weighted (+1.01% per year; $P<0.08$) and flow weighted (+1.08% per year; $P<0.24$) total N concentrations during 1991–2009 (Fig. 3-7; Table 3-2). Flow remained similar and did not show any significant trends ($P<0.75$) during 1991–2009. Therefore, the possibility of concentration or dilution of total N with variations in the natural causes (flow) is ruled out. Non-significant trends

in flow weighted concentrations could be due to greater variations in flow resulting in greater variance in data and therefore non-significant results (Johnson et al., 2009). Similarly the loads data at Bell Shoals is insignificant due to greater variations in the data. Greater variation in the loads could be due to the large variation in smaller streams of the Alafia River Watershed. However, increasing trends in both flow weighted and flow un-weighted total N concentrations indicated the possibility of anthropogenic influence in increasing the N concentrations in the Alafia River. In this regard, the Alafia River Watershed is similar to most of the watersheds in US which have shown increasing total N concentration trends during the last few decades (Goolsby and Battaglin, 2001; Turner and Rabalais, 2003; Weston et al., 2009). For example, in Mississippi River Basin, Turner and Rabalais (2003) reported the increasing total N concentration trends primarily due to clearing of forests for the agricultural land use in the last 200 years. Similarly, in Minnesota River, Mann-Kendall trend analysis showed increasing NO_3-N concentration trends (from +2.90 to +6.29% per year) during 1976–2003 (Johnson et al., 2009). They attributed the increasing N losses to the increased drainage of the corn-soybean dominated watersheds during 1976–2003. Contrary to these studies, in 58 watersheds of Eastern US, Sprague and Lorenz, (2009) using Mann-Kendall trend analysis have not found any significant total N concentrations trends during 1993–2003.

In the Alafia River Watershed which is located in the Hillsborough County, population has grown from 0.83 million in 1990 to 0.99 million in 2000 and 1.20 million in 2009 (US Census Bureau, 2010). This represents 19.8% increase during 1990–2000 and 19.7% during 2000–2009. The population growth has resulted in the land use changes in the watershed. For example, the urban land use (residential and built up) has increased by 8% (from 12 to 20%) of the watershed during 1990–2007 (SWFWMD, 2007). This is coupled with a decrease of 5% in forests (from 23

to 18%) and 8% decrease in pastures (from 19 to 11%) while agricultural land use remained similar (8%) during the study period. In our study, mean total N concentrations were positively correlated with urban (r=0.83) (Fig. 3-11; Fig. 3-12). Therefore, increasing trends of total N concentration in the Alafia River Watershed may be attributed to the increase in urban land use of the watershed. Similarly, studies in the Altamaha River, GA by Weston et al., (2009) reported the significant increasing total N trends (+7.42 µg L^{-1} per year) during 1970–2000. In their study, the average population density was increased from 35 to 70 person km^{-2} while the agricultural land use had decreased from 44 to 29%; thereby reflecting the impact of urbanization on total N losses. In general, the increase in urban land use results in increase in the N inputs (fertilizer application to lawns, septic tanks, leaf litter, and grass cutting of lawns) and changes the hydrology of the watershed which can increase the N losses to the streams (Carpenter et al., 1998; Han et al., 2009; Tufford et al., 1998). In our study, two developed sub-basins (English Creek and North Prong) have shown the decreasing total N concentration trends where the urban land use has increased by 8–23% during 1990–2007. It is important to note that at sub-basin scale several anthropogenic changes takes place simultaneously which affect the net N losses from a watershed. For example, N concentrations in streams may increase with the urbanization in the watershed while the improvements in the wastewater treatment facilities might decrease N losses resulting in decreasing or non significant results (Sprague and Lorenz, 2009). Two sub-basins (North Prong and English Creek) receive discharges from two domestic wastewater discharges in additions to several small industrial wastewaters (NPDES, 2009). We believe that in English Creek and North Prong the increasing total N concentration trends due to urbanization are offset by the improvements in the domestic as well industrial wastewater discharges.

In our study, NO_3-N (25–68% of total N) has not any significant increasing or decreasing trends at all the study stations (Fig. 3-9). Among the sub-basins, only Turkey Creek has shown the increasing flow un-weighted NO_3-N concentration trends during 1991–2009. In the Alafia River Watershed, several programs such as fertilizer application based on crop/soil tests, N pollution reduction from residential areas, improvements in wastewater treatment facilities were initiated to control N (especially NO_3-N) pollution during last two decades (TBEP, 2009). It seems the success of the N abatement programs is partially offset by the increasing urban land use and population growth resulting in insignificant NO_3-N concentration trends during the study period. In contrast to NO_3-N, the ON which contributed 30–71% of total N, has shown significantly increasing trends most of the study stations (Fig. 3-8). In general, increasing ON concentration trends due to increases in urban land use in the Alafia River Watershed contradicts the common belief that urban land use increase the NO_3-N rather than ON losses from watersheds (Pellerin et al., 2006; Stanley and Maxted, 2008). In our study, the proportion of ON decreased with increasing urban land use while the concentrations of ON were similar in both developed and undeveloped sub-basins. This suggests that there are sources of ON even in the urban land uses. In urban land uses, the impervious areas increase the runoff resulting in greater transport of particulate ON which may ultimately lead to increasing ON concentration trends with urbanization (Carpenter et al., 1998; Han et al., 2009; Tufford et al., 1998). In a review of 348 watersheds, Pallerin et al. (2006) reported that the ON concentrations in the surface waters were 2-3 folds greater in urban/suburban (0.47–0.49 mg L^{-1}) than forest watersheds (0.18 mg L^{-1}). They attributed the greater concentrations in urban land uses to the influence of septic tanks, wastewater treatment plants, and the biotic conversions of NO_3-N to ON. Using isotopic signatures of carbon and N, Peebles et al. (2009) reported that inorganic N from the fertilizers

was the dominant source of N to the sediments in the Safety Harbor part of the Tampa Bay. Similarly, long-term N fertilization studies at the Harvard Forest in Massachusetts have shown that dissolved ON concentrations in the forest floor have increased as a result of elevated inorganic N deposition (McDowell et al., 2004). In our study, wetlands and artificial retention ponds might have played a stimulating role for biotic conversion of NO_3-N into ON which resulted in increased ON concentration trends with urbanization during the study period (Groffman et al., 2004; Pellerin et al., 2004). In this way, increasing ON concentration trends in this urbanizing watershed has raised two important questions 1) Is the increase in ON concentration due to ON sources (such as septic tanks, urban manures/composts, runoff of grass cuttings, and deciduous leaves fallen on the urban surfaces, 2) Is the ON increase a product of microbial transformations of NO_3-N into ON. Further studies on the source characterization of the ON can help in devising the BMP's to control N pollution in the Alafia River Watershed.

Results of our trend analysis suggested that the increasing total N concentrations could be due to the increasing urban land use in the watershed during 1991–2009. None of the sub-basin showed significant decreasing or increasing NO_3-N trends. This has suggested that the conversion from forest and pastures to urban land use has offset the success of the N abatement programs in controlling NO_3-N pollution in the Alafia River Watershed. On the other hand, lack of BMP's to target ON (30–71% of total N) has caused increase in ON concentrations ultimately resulting in increasing total N trends. For controlling N pollution, Turkey Creek with greater total N concentrations and increasing total N concentration trends should be targeted followed by English Creek to control N pollution. In these two developed sub-basins, the BMP's should also focus ON rather than NO_3-N alone to protect water quality in the Alafia River Watershed.

Summary

At two mainstem stations (Alafia and Bell Shoals) that drain 89–99% of the Alafia River Watershed, the mean total N concentrations approached the EPA proposed numeric total N criteria values for the region. During 2000–2009, total N concentrations were greater in three developed (1.67–2.43 mg L^{-1}) than two undeveloped sub-basins (0.84–1.21 mg L^{-1}) thereby suggesting that the urbanization of the watershed has increased N losses from watersheds. Greater proportion of NO_3-N in developed (53–68% of total N) than undeveloped sub-basins (25–30%) indicate that in urban land uses the losses of NO_3-N are greater than ON. In our study, the concentration of NO_3-N decreased in wet season due to greater biotic uptake and denitrification of NO_3-N with greater temperature as well as dilution of NO_3-N with greater runoff in wet than dry season. The greater concentrations of ON in wet than dry season were probably due to greater transport of organic material with runoff water. The trend analysis showed increasing total N concentration at the mainstem station during 1991–2009. This was primarily due to the greater increases in ON than NO_3-N thereby suggesting the need to control N losses from ON sources. Three developed sub-basins (Turkey Creek, English Creek, and North Prong) that had greater total N concentrations should be first targeted to reduce N pollution in the Alafia River Watershed.

Table 3-1. Station characteristics of the Alafia River Watershed

Sub-basin	Station	Sampling location		Drainage area		Land Use in 2007					
		Lat	Long	km^2	%	Residential	Built up	Agricultural	Pasture	Forest	Mined
					Mainstem Stations						
Alafia	2301718	27.87	–82.32	1072	99	17	3	8	11	18	32
Bell Shoals	2301638	27.86	–82.26	974	89	16	3	8	12	18	33
					Developed						
English Creek	-†	27.93	–82.06	99	9	21	14	19	23	25	3
Turkey Creek	-†	27.91	–82.18	128	13	20	3	24	16	12	0
North Prong	2301000	27.86	–82.13	350	32	18	6	4	5	16	39
					Undeveloped						
South Prong	2301300	27.86	–82.13	277	26	3	1	4	9	15	66
Fishhawk Creek	†	27.85	–82.24	70.6	7	11	3	14	23	32	0

-† USGS station not present

Table 3-2. Long-term trends in flow weighted and loads of N forms at Bell Shoals

Parameter	data	Flow weighted concentrations			Loads		
		Trend	Slope (%)	p value	Trend	Slope	p value
Total Nitrogen	1991–2009	Increasing	+1.01	0.242	No trend	–	0.746
Organic Nitrogen	1991–2009	Increasing	+1.08	0.016	–	–	–
Nitrate Nitrogen	1991–2009	No trend	–	0.491	–	–	–

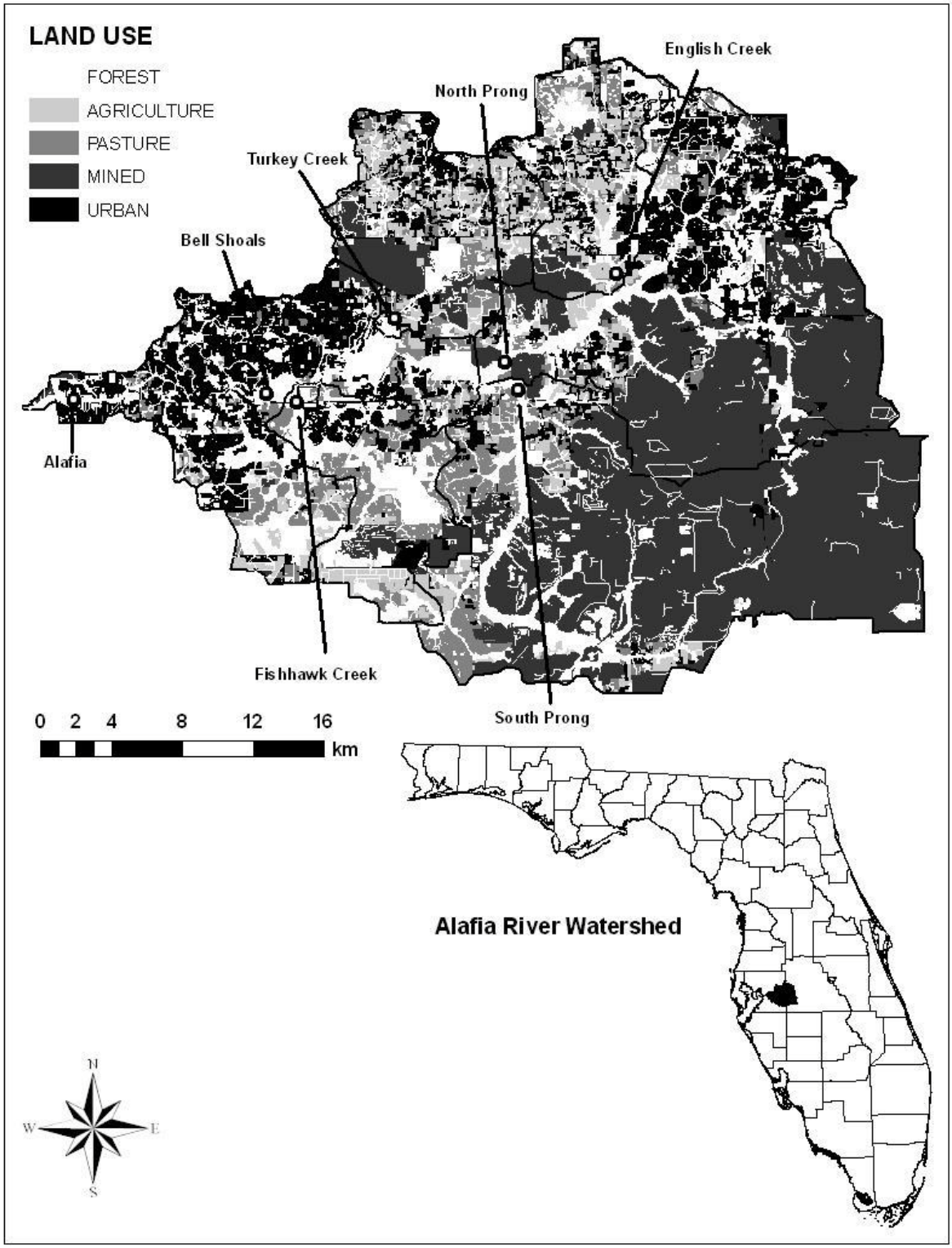

Figure 3-1. Location map of the Alafia River Watershed.

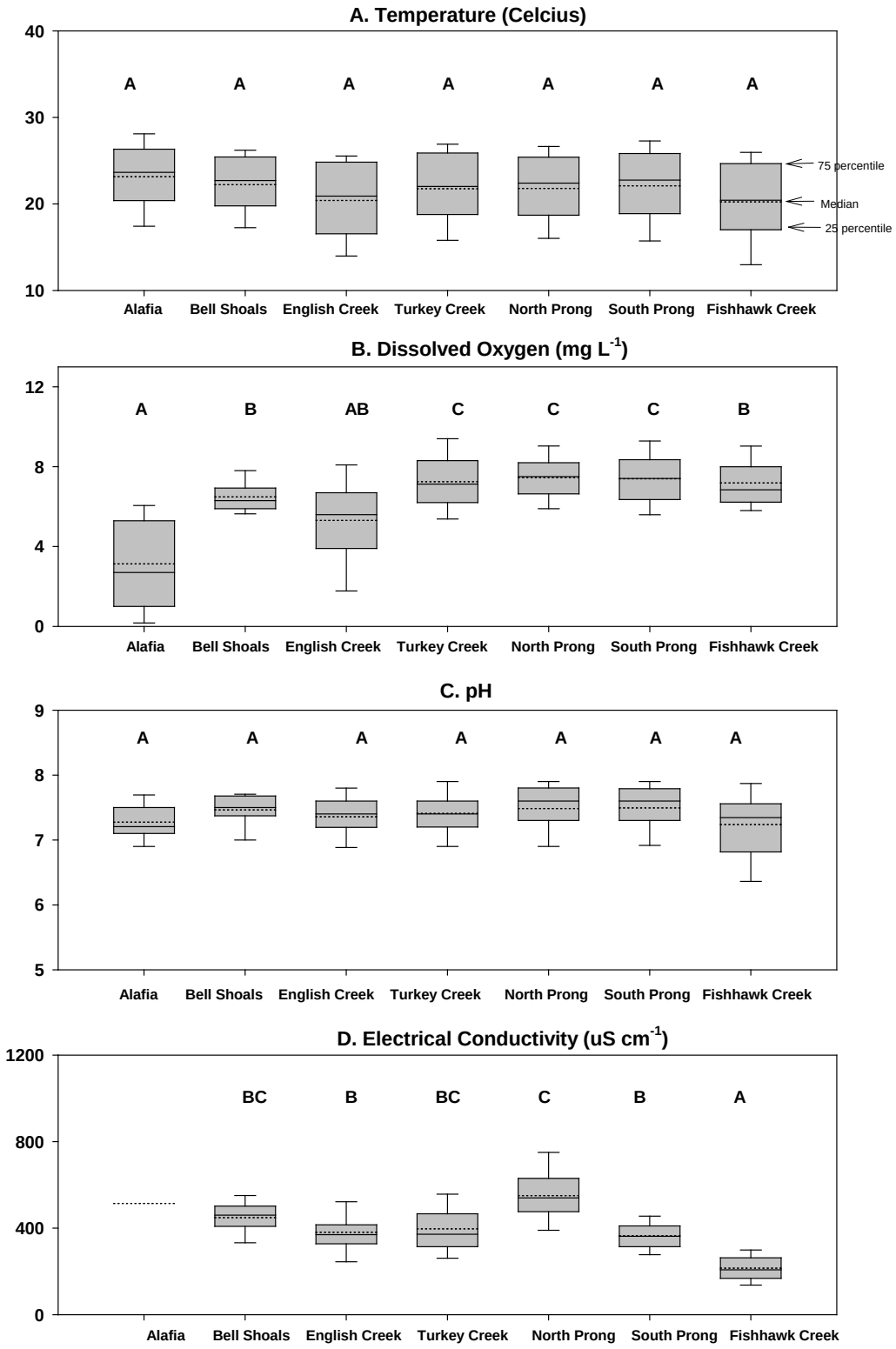

Figure 3-2. Chemical characteristics of the stream waters during two time periods from 1991 to 2009. Values indicated by different letters are significantly different at $P<0.05$ for each graph.

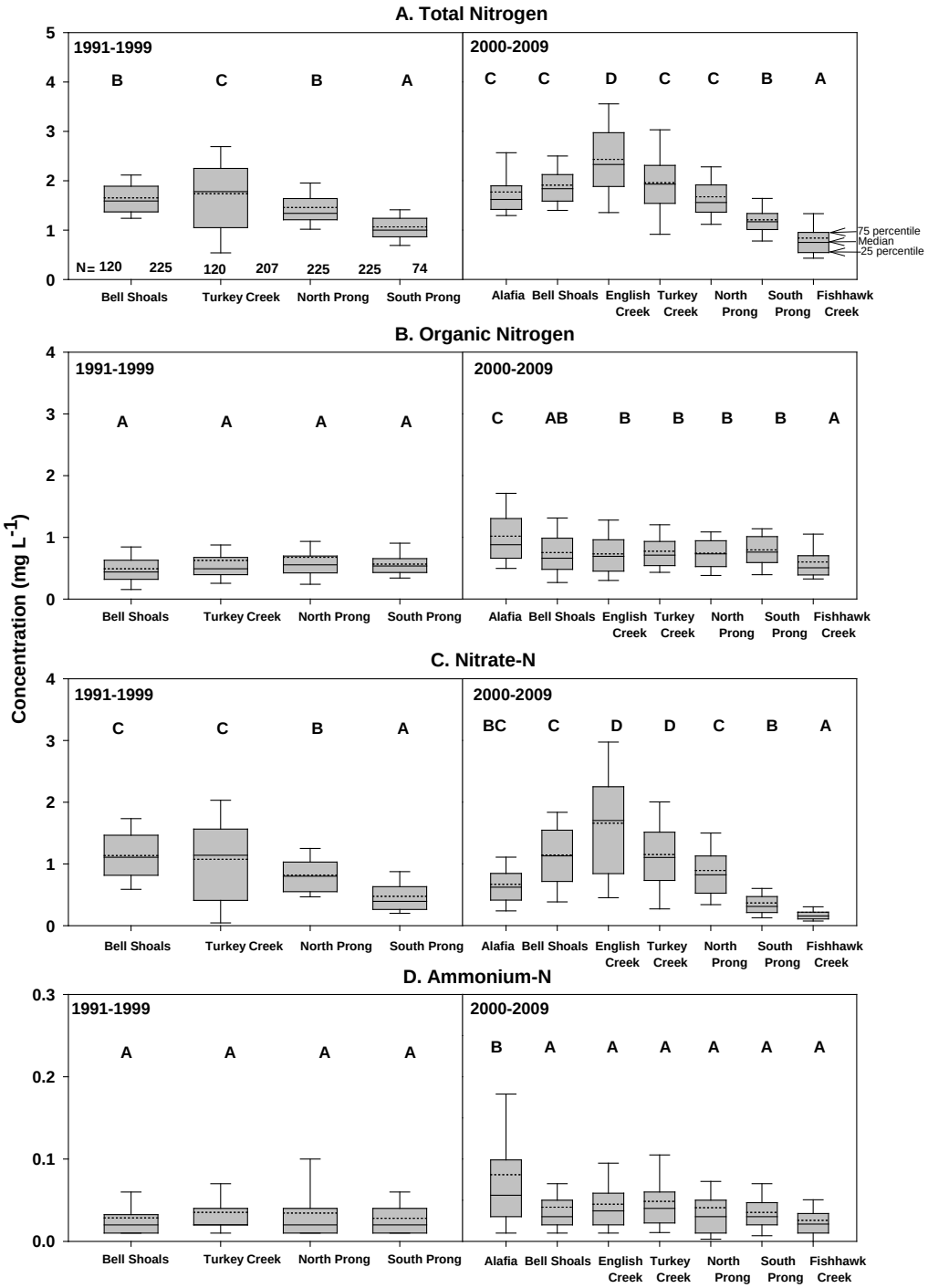

Figure 3-3. Summary of mean monthly concentrations of total, organic, nitrate, and ammonium nitrogen during 1991–2009 in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek). Values indicated by different letters are significantly different according to GLIMMIX procedure at $P < 0.05$. N in each sub-basin indicates number of months/observations.

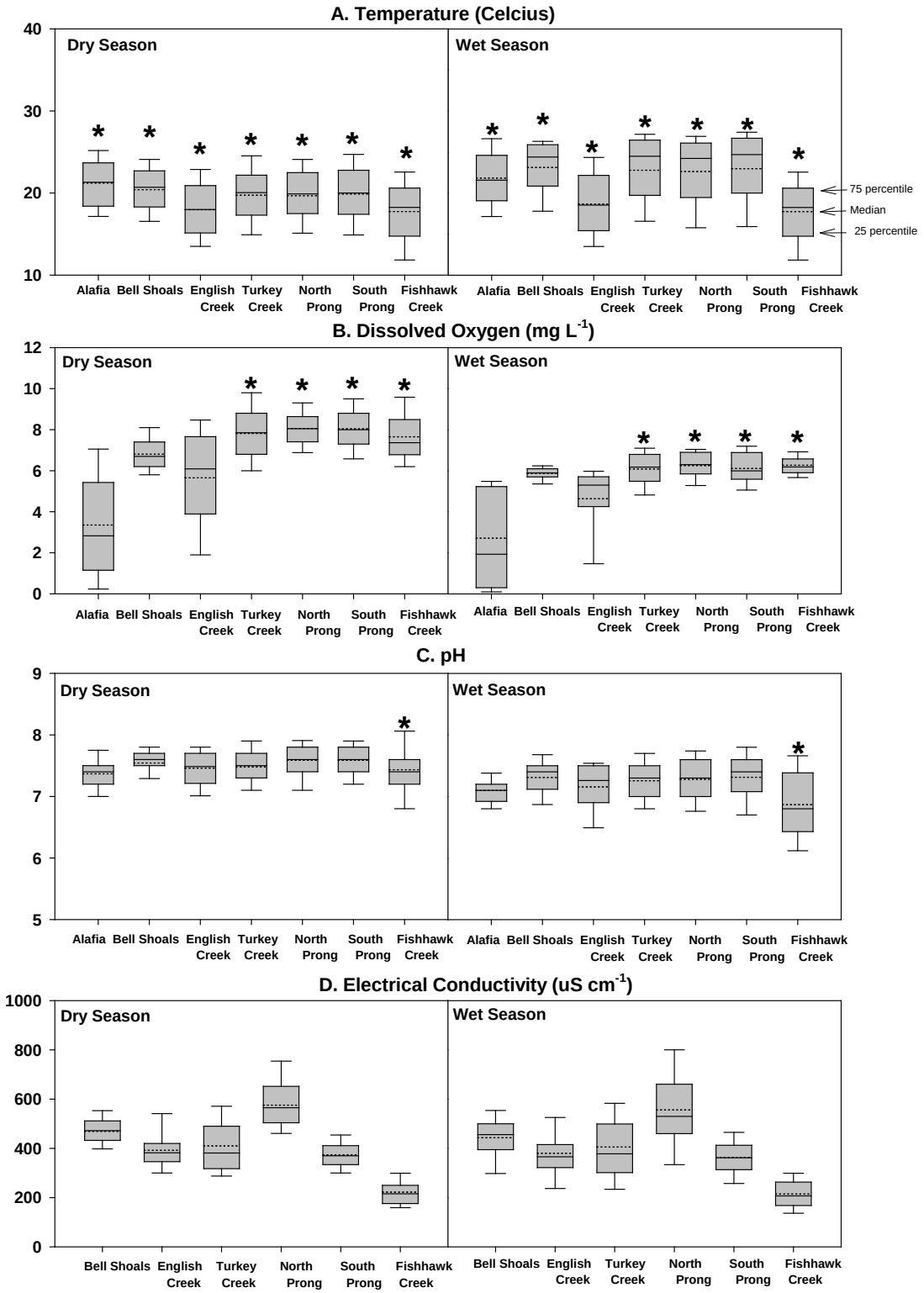

Figure 3-4. Seasonal variation in chemical characteristics of the stream waters during 1991–2009. Values indicated by different letters are significantly different according to GLIMMIX procedure at P< 0.05. Dotted line represents the mean value.

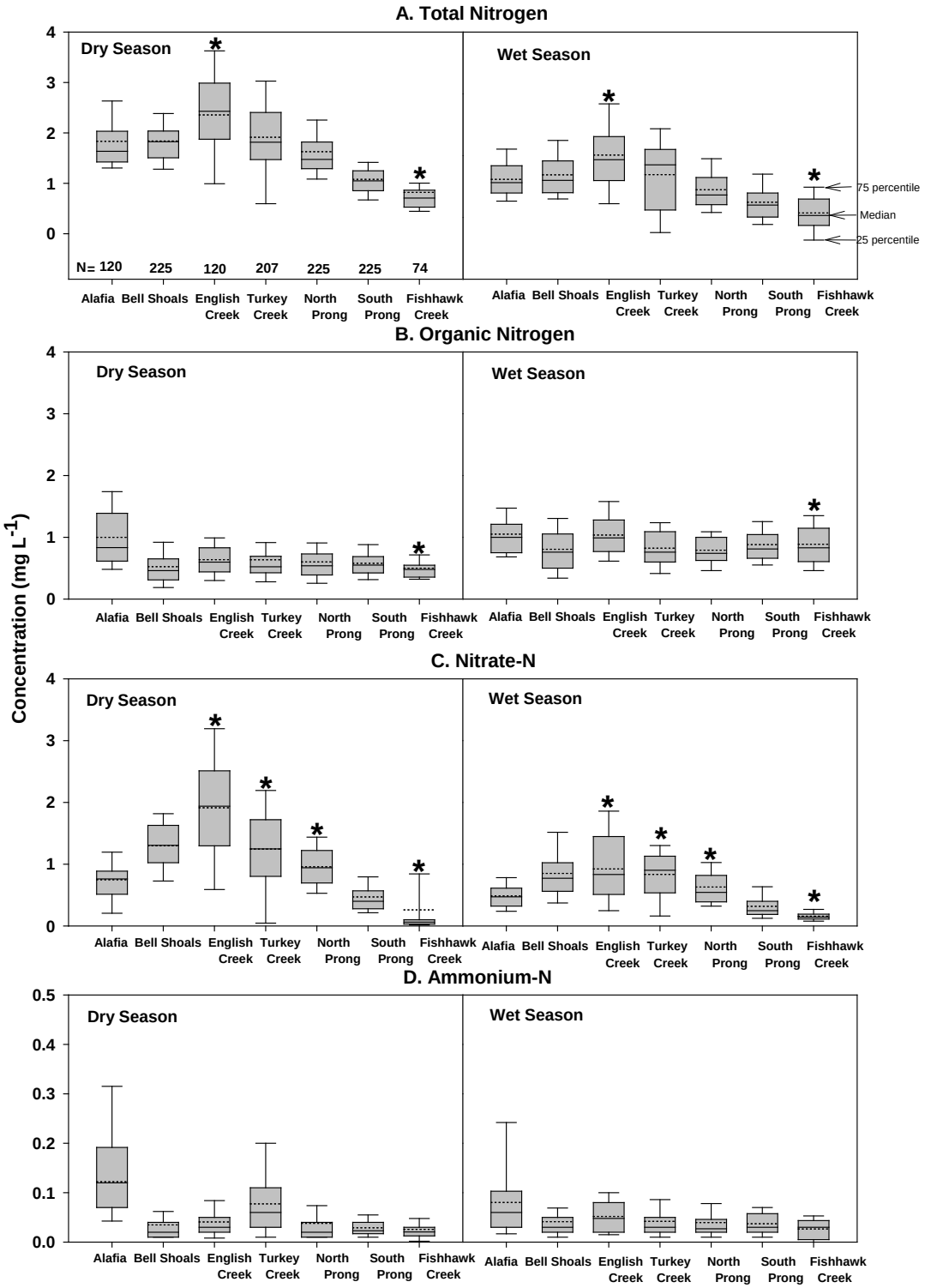

Figure 3-5. Seasonal variation in mean monthly concentration of nitrogen forms during 1991–2009. Values indicated by different letters are significantly different according to GLIMMIX procedure at P< 0.05. Dotted line represents the mean value.

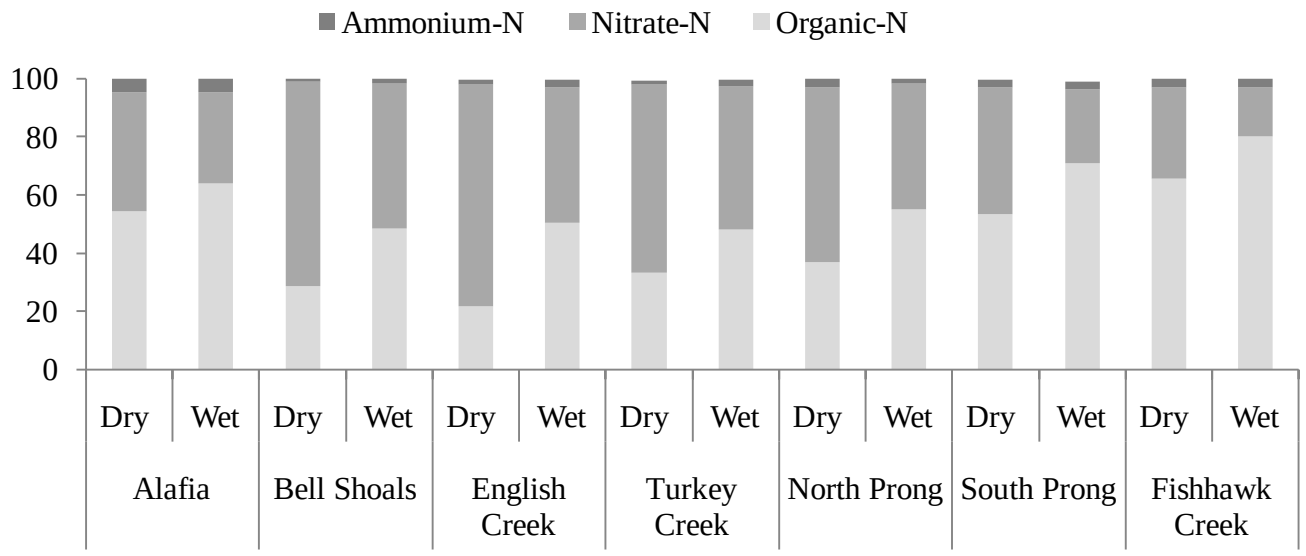

Figure 3-6. Seasonal variation in proportion of organic, nitrate, and ammonium nitrogen during 1991–2009.

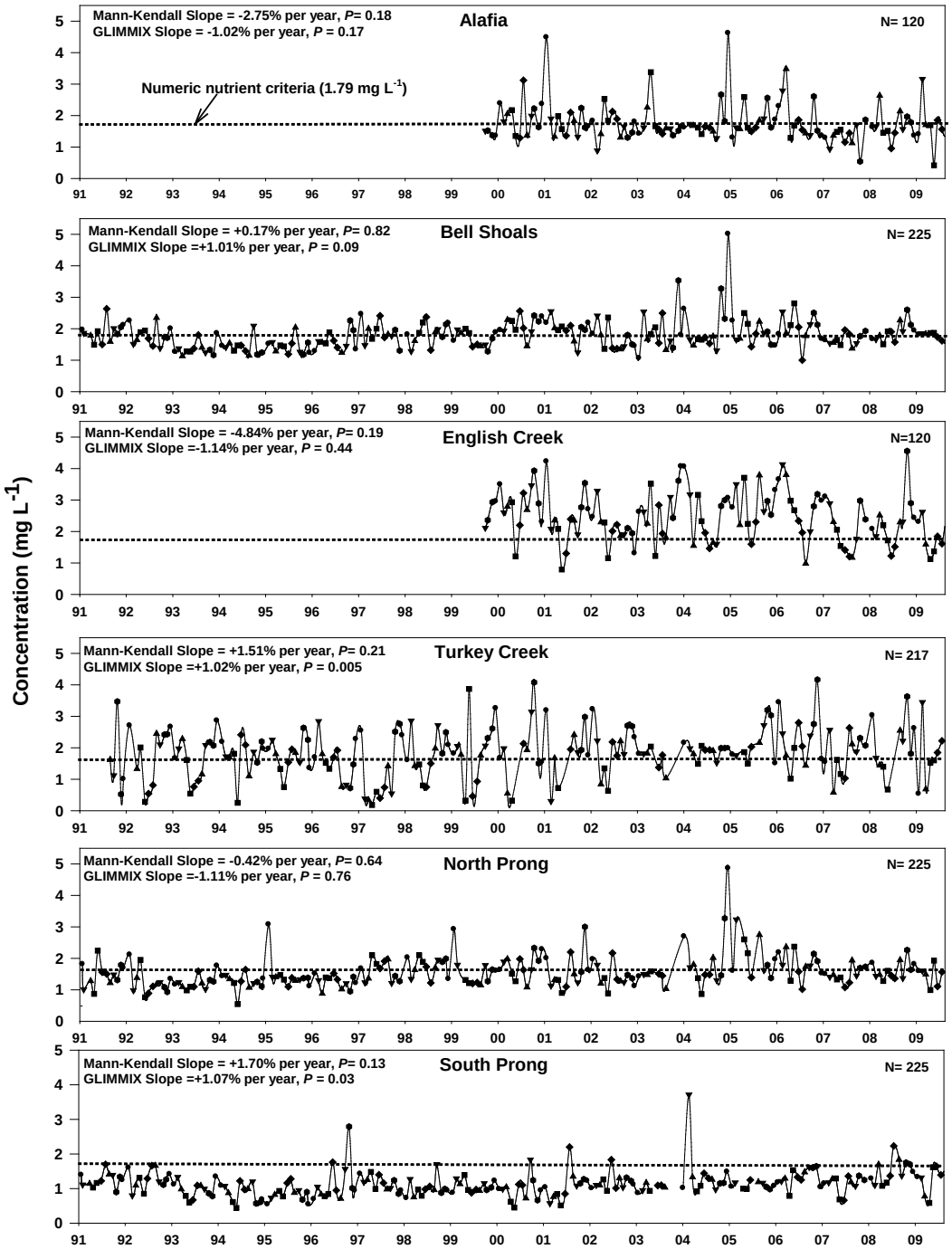

Figure 3-7. Long-term (1991–2009) trends in monthly flow un-weighted total N concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed. The dotted line indicates the proposed numeric nutrient (1.79 mg L^{-1}) criteria for the region (EPA, 2010).

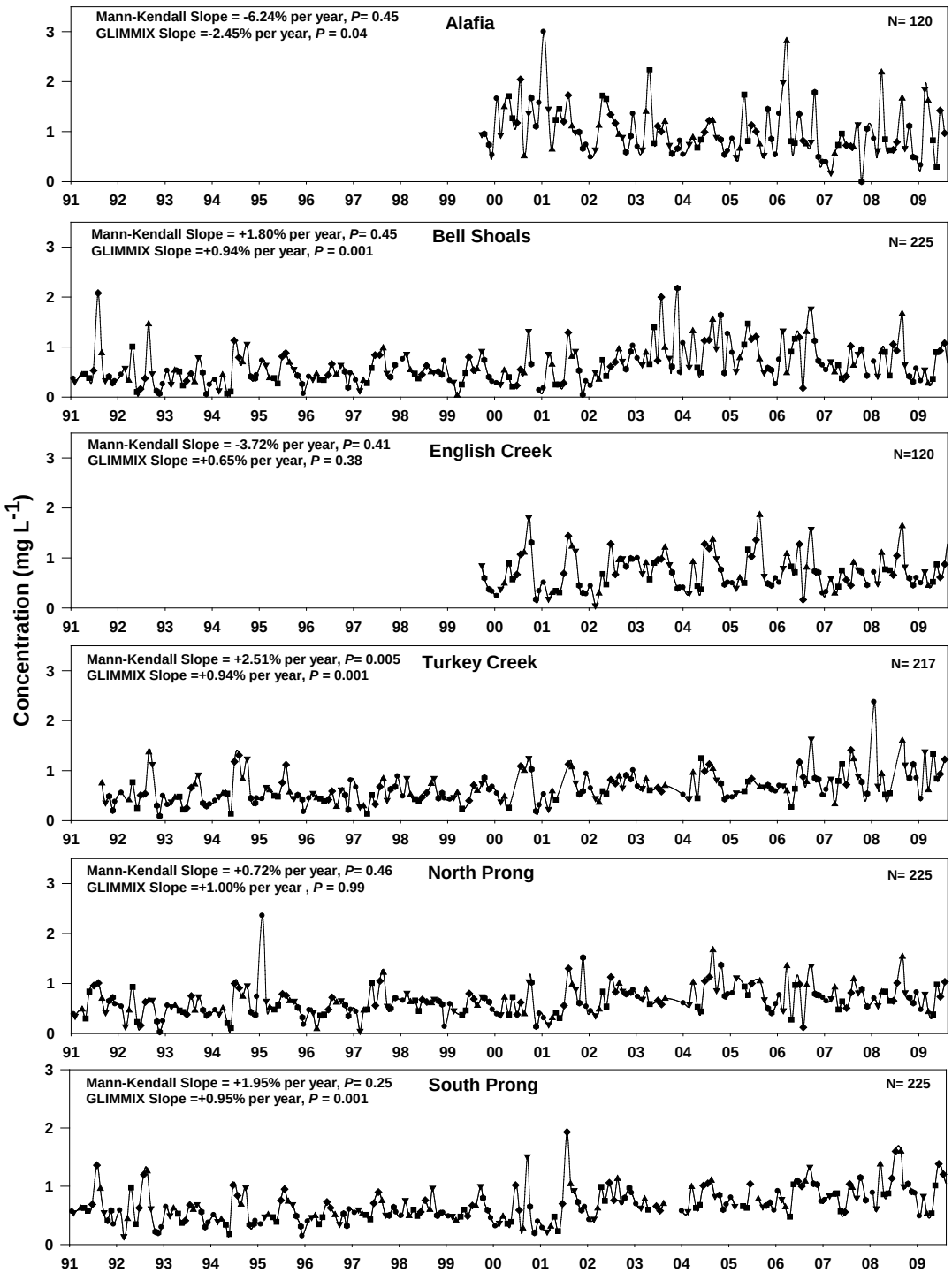

Figure 3-8. Long-term (1991–2009) trends in monthly flow un-weighted organic N concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed.

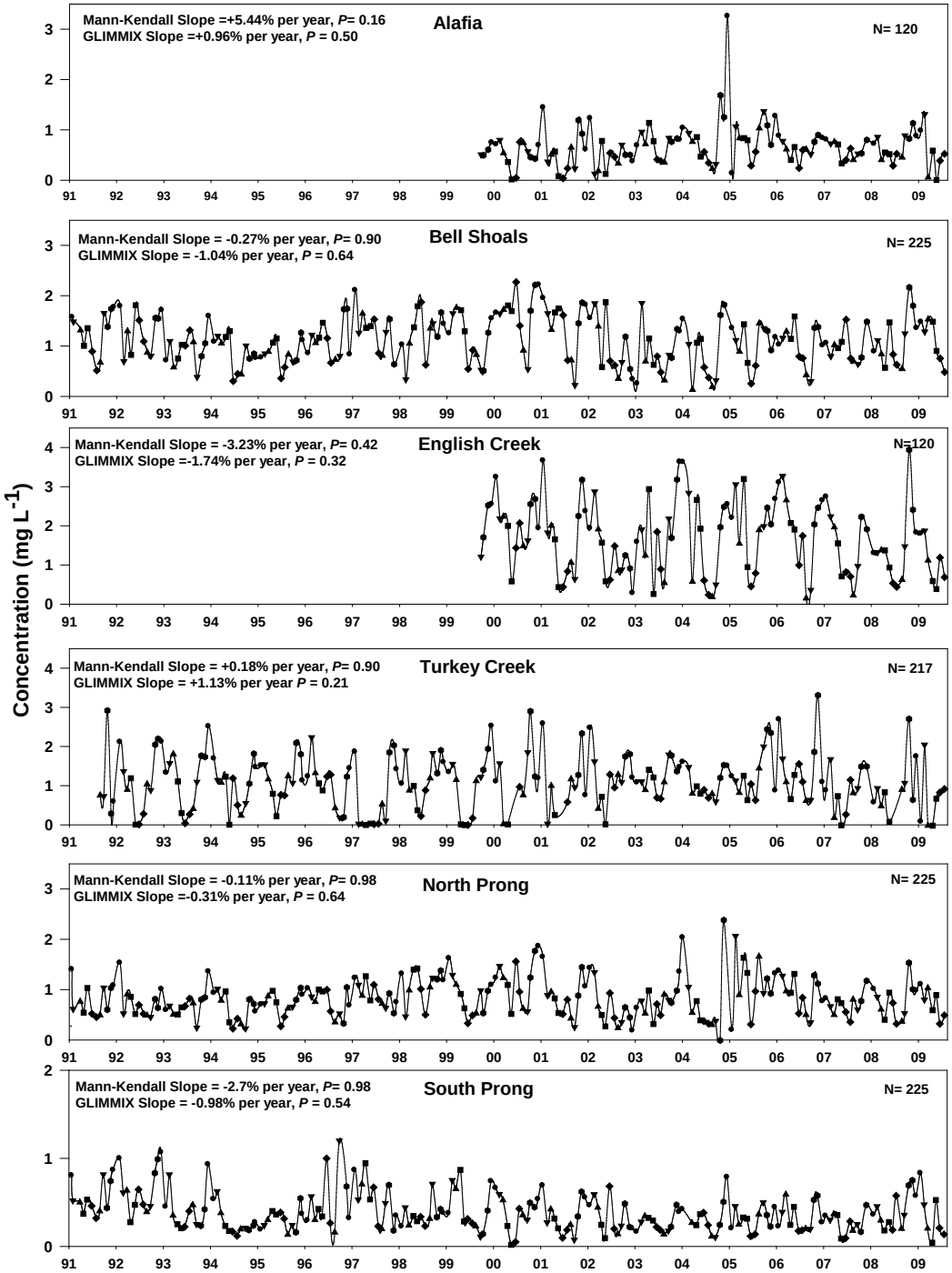

Figure 3-9. Long-term (1991–2009) trends in monthly nitrate N concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed.

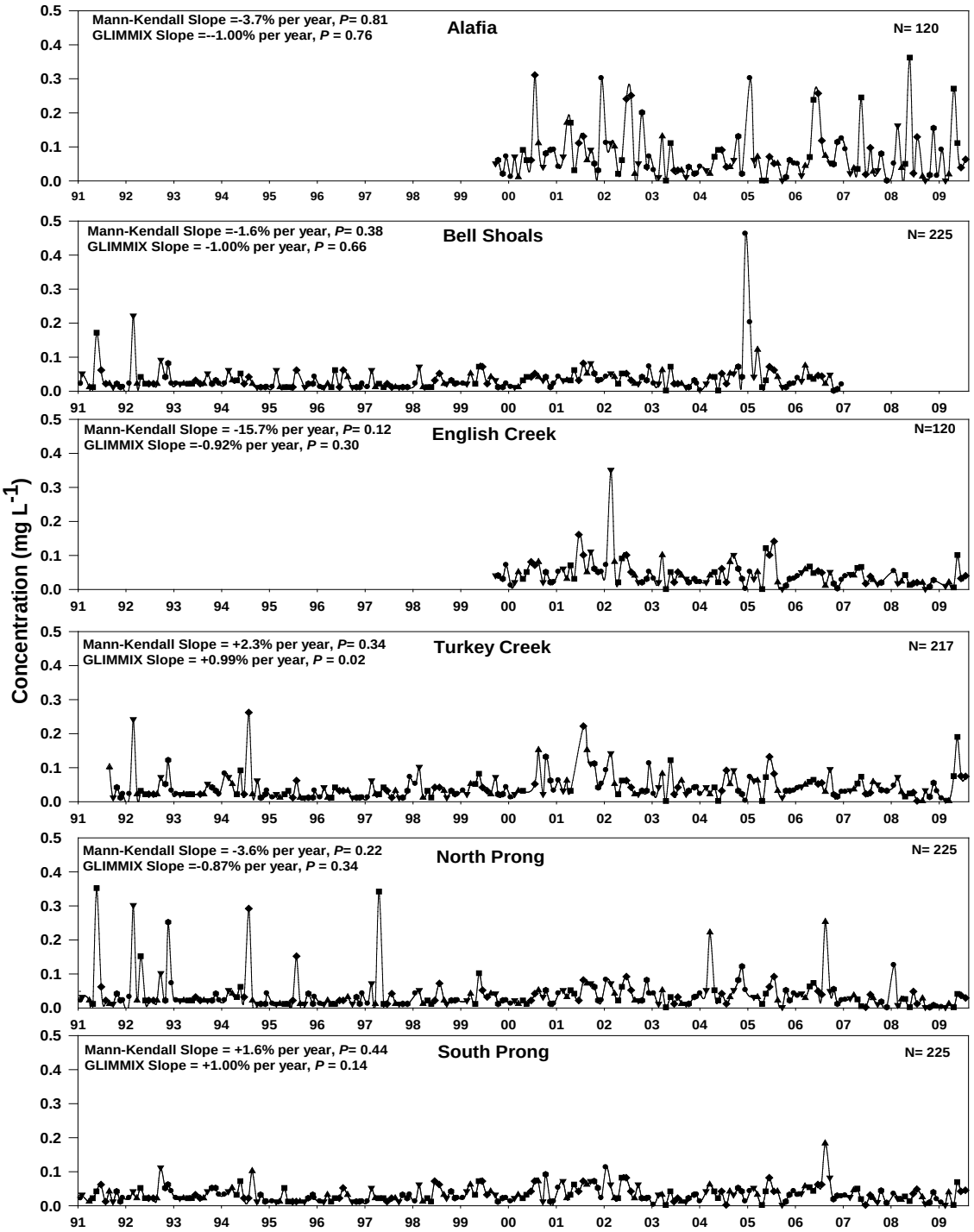

Figure 3-10. Long-term (1991–2009) trends in monthly flow un-weighted ammonium N concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed.

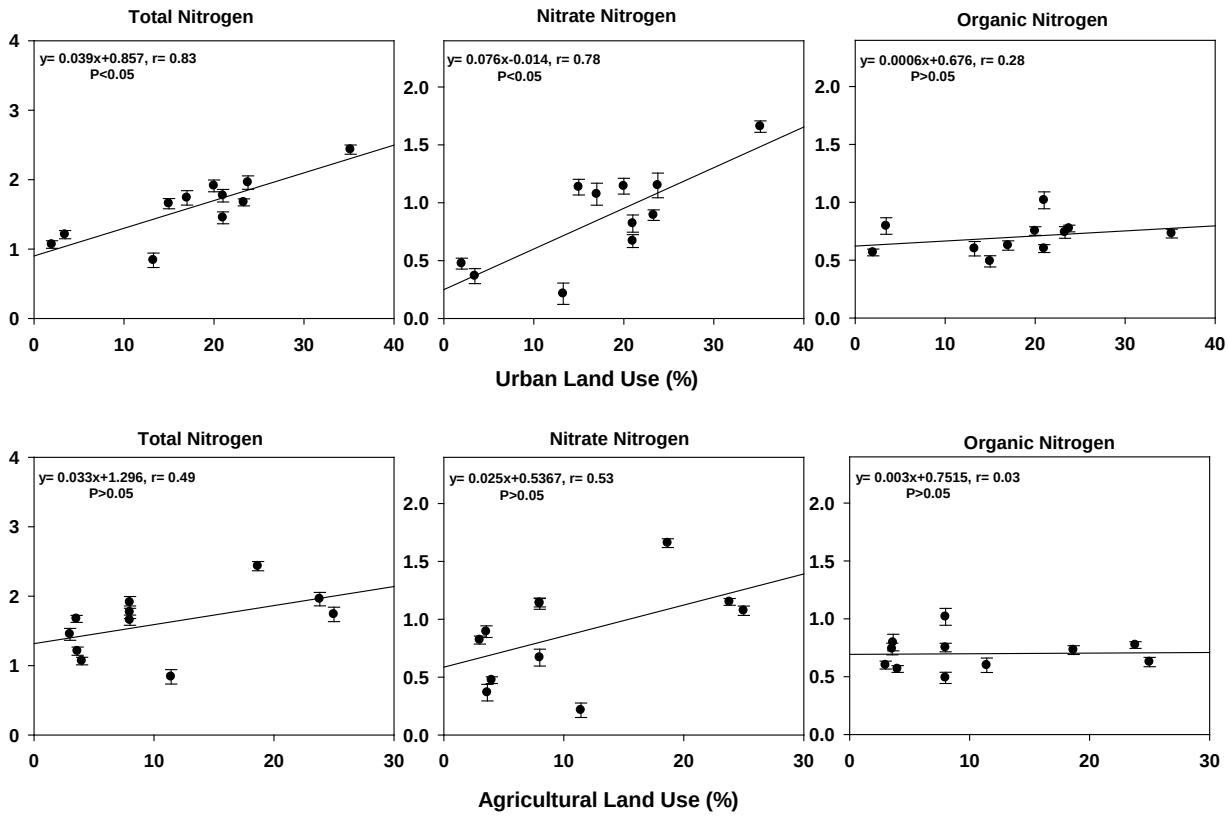

Figure 3-11. Relationship between percent urban and agricultural land use and nitrogen forms in different sub-basins (* significantly correlated at P< 0.05). Mean monthly data of 1991–1999 and 2000–2009 with land use of 1999 and 2007 respectively.

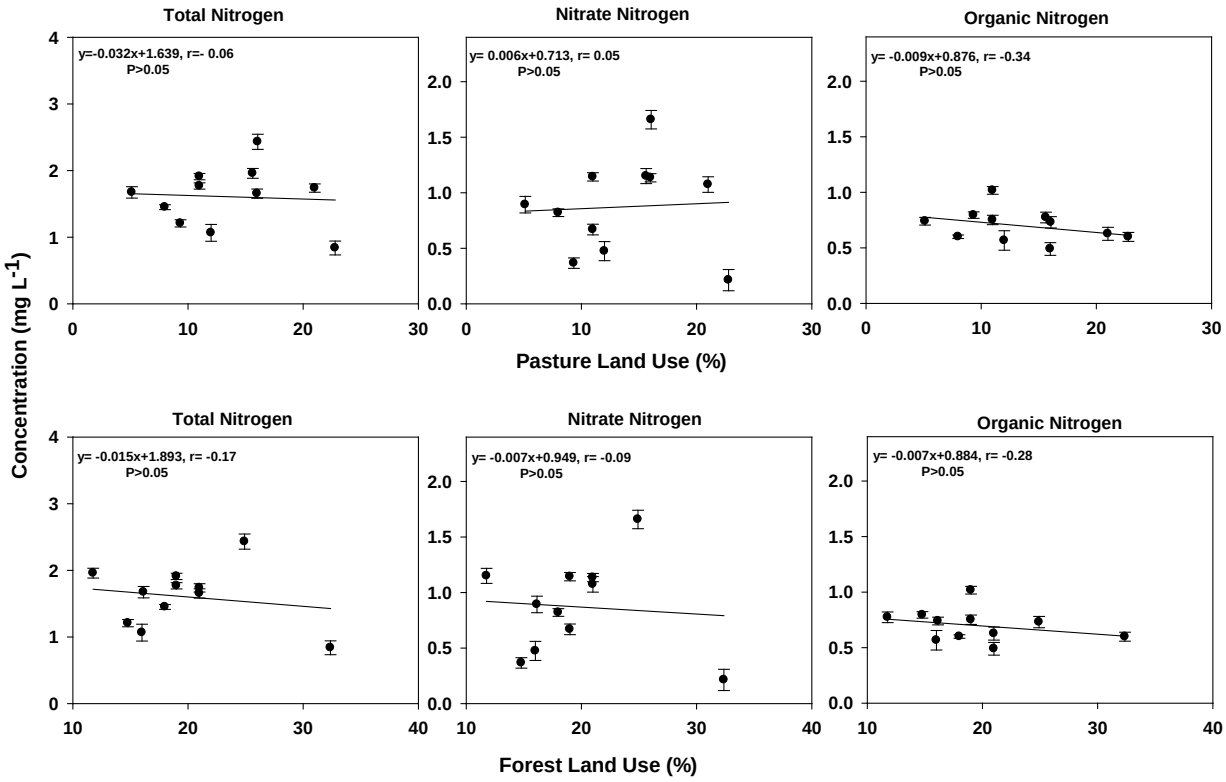

Figure 3-12. Relationship between pasture and forest land use and nitrogen forms in streams draining different sub-basins (* significantly correlated at $P < 0.05$). Mean monthly data of 1991–1999 and 2000–2009 with land use of 1999 and 2007 respectively.

CHAPTER 4
PHOSPHORUS TRANSPORT IN AN URBAN WATERSHED

Abstract

Non point source phosphorus (P) pollution is a significant concern in several waterbodies. In this study, we determined the concentrations of total P, dissolved reactive P (DRP), and other P forms in stream waters draining developed and undeveloped sub-basins, ranging in size from 19 to 350 km^2, of the Alafia River Watershed (total drainage area: 1085 km^2). During 1991–2009, mean monthly total P concentrations ranged from 0.56 to 3.95 mg P L^{-1}. Of total P, dissolved reactive P (DRP) was dominant (70–90% of total P) than other P (10–30% of total P) in developed and undeveloped sub-basins. None of the P forms were significantly ($P< 0.05$) correlated with urban, agricultural, forest, and pasture land use of the sub-basin ($r<0.50$) indicating that the P concentrations are not controlled by land use of the Alafia River Watershed. Greater concentration of total P were greater in two developed (North Prong and English Creek: 2.18–2.53 mg P L^{-1}) may be due to P rich geology, active mined lands, and discharges of P rich wastewater in these sub-basins. In all the developed and undeveloped sub-basins, the concentrations of P forms were greater in wet than dry season. This represents that the flushing of the P with greater rainfall-runoff in wet season that might have accumulated due to dissolution and desorption of P from soil minerals. Long term trend analysis showed decreasing total P and DRP trends in both flow weighted and flow un-weighted concentrations. The decreasing trends in P concentrations indicated that the P abatement programs such as increased regulations on P discharges from mined lands as well as wastewater discharges were successful in controlling P pollution in the Alafia River Watershed. During 2000–2009, all the sub-basin except Fishhawk Creek had greater total P concentrations (0.80–2.53 mg P L^{-1}) than EPA proposed numeric total P value of 0.739 mg L^{-1} for the region. Results suggests that P source controls from mined and

wastewater discharges in North Prong, English Creek, Turkey Creek, and South Prong are needed to control P pollution in the Alafia River Watershed.

Introduction

Phosphorus (P) pollution is the primary source of water quality degradation in the US (Bricker et al., 1998; USEPA, 2001) as total P concentration as low as 0.050 mg P L^{-1} in lakes and 0.10 mg P L^{-1} in stream waters can impair the water quality (USEPA, 1986). In the US, 45% of lakes and 35% of rivers are degraded and approximately 90% of the rivers show signs of eutrophication due to P enrichment (USEPA, 1996, 2000; Dodds et al., 2009; Paerl, 2009). The consequences of eutrophication include hypoxia, acidification of natural waters, degradation of coastal waters including increased episodes of noxious algal blooms, and reductions in aquatic macrophyte communities often leading to substantial shifts in ecosystem structure and function (Carpenter et al., 1998; Dodds et al., 2009). The cost of eutrophication has been estimated at $2.2 billion per annum due to losses of recreational water usage, spending on recovery of threatened and endangered species, and drinking waters (Dodds et al., 2009). Therefore, controls on the sources of P can help to protect the water resources and reduce water quality deterioration in a region.

Phosphorus in water bodies can come from either point sources such as wastewater and industrial effluents or non-point sources which include the storm water runoff losses from urban areas, agricultural fields, animal feedlots, roadways, and mined areas (Edwards and Withers, 2008). Following the passage of Clean Water Act in 1970, P contributions from the point sources have decreased and consequently non-point source has become the dominant form of P pollution in many watersheds in the US (Bricker et al., 1998; USEPA, 2001; Diebel et al., 2009; Maxted et al., 2009). A logical approach to control non-point P pollution may be to determine the hot spot areas that contribute greater P losses and to develop best management practices (BMPs) to

reduce P pollution from these hot spots (Haygarth, 2005). In Wisconsin, US, Diebel et al. (2009) reported that targeting 10% of watersheds decreased total P losses by 20% for the entire state. Therefore, federal, state and local government, nonprofits (e.g., The Nature Conservancy), and stakeholder groups (e.g., watershed associations, soil and water conservation districts) find watershed scale pollution assessment valuable for identifying and targeting the land areas which contribute greater pollution (hot spots) in a watershed.

In order to identify the hot spots areas at a watershed scale, it is vital to fully understand how different land uses impact non-point P pollution in a watershed. In general, land use affects the net anthropogenic inputs of P in watersheds. For example, Russell et al. (2008) reported that net anthropogenic P inputs were greater in agricultural and urban land uses (15.8–19.6 kg P ha^{-1}) as compared to forest watersheds (1.6 kg P ha^{-1}). Another consequence of the land use change is the alteration of the flow paths. For example, in urban watersheds, impervious surfaces lead to increased runoff due to altered hydrology compared to forest watersheds (Arnold and Gibbons, 1996; Lee and Heaney, 2003; Paul and Meyer, 2001). In this way, urban land uses result in greater flows and facilitates the transport of suspended solids, an important P transport source (Mulliss et al., 1996; Stone and Droppo, 1994). Further, the loss of natural vegetation in urban land uses reduces recycling and uptake of P by vegetation that can immobilize P (Abelho, 2001; Wahl et al., 1997). This can result in a greater amount of P available and thus export to water bodies in urban land use dominating watersheds.

The influence of land use on P exports from watersheds can be seen in Lake Washington, US, where Ellison and Brett, (2006) reported greater total P concentrations in streams draining agricultural (0.13 mg P L^{-1}) and urban (0.07 mg P L^{-1}) than forest sub-basins (0.03 mg P L^{-1}). Similarly, in 17 watersheds dominated with urban (22–87%) or forest (6–73%) land use, Brett et

al. (2005) reported that with 10% conversion of forest to urban land use, total P concentrations increased by 0.07 mg P L^{-1}. In contrast to these studies, other researchers have not observed any significant difference in P losses from different land use dominated watersheds (Dodds and Oakes, 2006; Johnson et al., 1997). Therefore, losses of P may or may not be impacted by land uses in a watershed despite the fact that land use alters inputs as well as mode of delivery of P from watersheds to streams.

Land use in a watershed may influence the proportion of the different P forms such as dissolved reactive P (DRP) and particulate P (PP) in the streams (Stone and Droppo, 1994). In general, PP losses are often associated with the erosion of soil particles that are enhanced by the anthropogenic land use and soil disturbance typical in agricultural dominated watersheds (Wallbrink et al., 2003). On the other hand, DRP in the stream waters represents the losses from the anthropogenic sources such as fertilizer application to the agricultural fields as well as to the weathering of the P minerals if present in a watershed (Harrison et al., 2005). Most of the studies have demonstrated that about 50% of the P losses occur as PP (Omernik, 1977; Sharpley and Menzel, 1987; Vaithiyanathan and Correll, 1992). However, in Lake Washington, Ellision and Brett (2006) reported that of total P, the total dissolved P was 72% in urban (0.05 mg P L^{-1}) and 60–64% in forest and mixed (0.02–0.04 mg P L^{-1}) compared to 50% (0.07 mg P L^{-1}) in agricultural streams. Information on the losses of different P forms from sub-basins under contrasting land use activities may act as a useful tool in studying the cycling of P, which may be valuable to develop source control of P in sub-basins draining different land uses.

In addition to the land uses, stream flow conditions affect the concentration and proportions of P losses from the watersheds (Ellison and Brett, 2006; Qian et al., 2007). For example, Royer et al. (2006) reported that in corn-soybean dominated (80–90%) watersheds in

Illinois, US, >80% of the total P losses occur only during the high flow conditions (>90% percentile flow). In Indian River Lagoon, Florida, Qian et al. (2007) reported that the concentrations of P forms were two times greater during wet (DRP: 0.23 mg P L^{-1}; total P: 0.31 mg P L^{-1}) than dry season (DRP: 0.11 mg P L^{-1}; total P: 0.15 mg P L^{-1}). In general, P is sorbed onto the soil particles and greater losses of P occur when sufficient water is available to transport soil particles from land to streams. In this way, ecological impacts due to P pollution may depend upon the flow conditions (Edwards et al., 2000; Jarvie et al., 2006; Svendsen et al., 1995).

The Alafia River Watershed is an example of such a watershed, where land use has been continuously changing from natural areas to urban lands. As a result, several sub-basins of the watershed have modified hydrology due to stormwater retention ponds and water convergence structures that are meant to drain water during high flow events to avoid flooding. In addition, two sub-basins of the watershed are dominant in mined lands where phosphate mining is a commercial enterprise. We hypothesize that the 1) concentration of P forms may be different in sub-basins that drain different land uses, 2) concentration of P forms may differ in dry and wet seasons due to difference in rainfall, and 3) urbanization of the watershed may increase the P concentrations. The objectives of this study were to (1) determine how different sub-basins (with different land uses) influence concentrations of different forms of P in stream waters; (2) investigate the influence of two distinct seasons (dry and wet) on concentrations of P forms in stream waters, and (3) evaluate the long term trends of P losses in different sub-basins of the watershed.

Materials and Methods

Study Site Description

Refer to Chapter 2 for detailed description of sub-basins of the Alafia River Watershed.

Data Collection

Monthly concentrations of total P, and dissolved reactive P (DRP) from 1991 to 2009 were obtained from the Environmental Protection Commission of Hillsborough County (http://www.epchc.org). Among the two mainstem stations, water quality data was available only for Bell Shoals station for 19-years study period, while for Alafia station, the data was available for 1999 to 2009 (Table 4-1). Among other sub-basins in the watershed, 19 years of water quality data were available only for North Prong, South Prong, and Turkey Creek while the data availability for English Creek was from 1999 to 2009 and for Fishhawk Creek from 2005 to 2009.

Stream-water Collection and Analysis

Each month, a grab sample from surface water was collected from the surface of channel thalweg (centre of the stream flow) in plastic water bottles by the EPCHC staff. Before collection of the samples, the water bottles were rinsed three times with the stream water. The collected samples were chilled with ice and transported to the laboratory where samples were stored at 4 ^{o}C prior to analysis. Environmental Protection Commission Hillsborough County staff analyzed the surface water samples for total P (EPA 365.4 method) and DRP (SM 4500-P method) using a discrete analyzer (Seal Analytical, Model AQ_2 Mequon, WI). Other P (OP) was calculated as follows: OP = total P–DRP.

Statistical Analysis

Mean, median, and standard deviations were calculated using MS Excel 2007. We used GLIMMIX time series procedure SAS Version 9.1 (SAS Institute, Cary, NC) to compare the P forms across different sub-basins as well as to determine the long term trends in P forms. The GLIMMIX procedure fits models to data with correlations or non constant variability and assumes normal random effects (SAS Institute, 2008). In this time series analysis two kinds of

effects were used 1) fixed effects which included stream station and season of the year, and 2) random effects, which were the date of sample collection. For the first fixed effect (stream station), each station was treated as a group and the variance was pooled over the sites; similarly for the second fixed effect (season), each wet (June–September) and dry (October–May) season at each station was treated as one group of observations. The date of sample collection from 1991–2009 for the each station was considered as random effect and therefore a time series was constructed. With this, we compared 1) the difference in P forms at each of the station averaged over all sampling dates and 2) differences in pooled mean concentrations of P forms during wet and dry seasons at each station using $P<0.05$ as significance level. In addition, same time series with fixed and random effects were used to determine the trends in P forms over the period of study. The concentrations of different forms of P were logarithmically transformed to equalize variances and normalize skewed data and were back transformed to present means of P forms in more relevant manner.

For the long term water quality data, various techniques have been used (Richards, 2006; Johnson et al., 2009; Goodrich et al., 2009). However, non parametric Mann-Kendall and Seasonal Kendall are among the most common methods for determination of long term trends of water quality (Daroub et al., 2009; Johnson et al., 2009). Therefore, in addition to GLIMMIX procedure, we determined the long term trends using Seasonal Kendall procedure. In Seasonal Kendall trend is calculated by comparing all potential data pairs. If the later value in the pair (in time) is higher than the first, a plus sign is scored. If the later value in the pair is lower than the first, a minus sign is scored. If the results find an equal number of pluses and minuses, then there is no discernible trend. In other words, there is just as much of a likelihood that a pair of data

values will be higher (or lower) than the next one. If the results show more pluses than minuses, this would indicate that a positive trend is likely (Gilbert, 1987; Helsel and Hirsch, 1991).

The trend in both the procedures is defined by the rate of change over time, which is referred to as the trend slope (Sen 1968; Schertz et al. 1991). The trend slope can be expressed either as change in original units per year [S (0)], or as a percent of the mean concentration of water quality variable [S (%)]. The former is the median slope of all pair wise comparisons (each pair wise difference is divided by the number of years separating the pair of observations) while the latter is produced by dividing the slope (in original units per year) by the mean and multiplying by 100.

The P forms concentrations data were divided into two time periods: 1991–2000 and 2001–2009. To determine the effect of land use change on P forms in corresponding sub-basins, the land use data of 1999 and 2007 was correlated with P concentrations data of 1991–2000 and 2001–2009, respectively, using SAS PROC CORR procedure.

Results

Chemical Characteristics of Stream Waters

Refer to Chapter 3 for detailed description of chemical characteristics of the stream waters.

Concentrations of Phosphorus Forms in Streams Draining Different Sub-basins

Mean monthly total P concentration at the mainstem station (Bell Shoals) that drains 89% of the watershed was 1.76 mg P L^{-1} during 1991–1999 (Fig. 4-2A). Among the sub-basins, total P concentrations were 4–5 folds greater in one developed (North Prong: 3.95 mg P L^{-1}) than one developed (Turkey Creek: 0.78 mg P L^{-1}) and one undeveloped (South Prong: 0.89 mg L^{-1}) sub-basin. The concentrations of total P decreased with time in the Alafia River Watershed (Fig. 4-2A). For example, at mainstem stations (Bell Shoals), mean total P concentrations were lower during 2000– 2009 (1.24 mg P L^{-1}) than 1991–1999 (1.76 mg P L^{-1}). Similar to the mainstem

station, at North Prong, South Prong, and Turkey Creek, the total P concentrations decreased from 0.9–3.9 mg P L^{-1} in 1991–1999 to 0.6–2.5 mg P L^{-1} in 2000–2009. Among the sub-basins, two developed sub-basins had significantly (P< 0.05) greater total P concentrations (North Prong and English Creek: 2.18–2.53 mg P L^{-1}) than one developed (Turkey Creek; 0.90 mg P L^{-1}) and two undeveloped sub-basins (0.56–0.80 mg P L^{-1}).

At the mainstem station (Bell Shoals), mean DRP concentration was greater (1.46 mg L^{-1}) during 1991–1999 than 2000–2009 (1.00 mg L^{-1}) (Fig. 4-2B). Similarly, at two developed (North Prong and Turkey Creek) and one undeveloped (South Prong), the concentration of DRP decreased from 0.8–3.3 mg L^{-1} in 1991–1999 to 0.7–2.2 mg L^{-1} in 2000–2009. During 2000–2009, all the three developed sub-basins had significantly (P< 0.05) greater DRP concentrations (North Prong, South Prong, and Turkey Creek: 0.63–2.18 mg P L^{-1}: 70–90% of total P) than one undeveloped sub-basin (Fishhawk Creek: 0.40 mg P L^{-1}: 72% of total P). However, North Prong and English Creek had 3–4 folds greater DRP concentrations (1.95–2.18 mg P L^{-1}) than Turkey Creek (0.63 mg P L^{-1}). Among the undeveloped sub-basins, South Prong had significantly (P< 0.05) greater total P concentration (0.68 mg P L^{-1}) than Fishhawk Creek (0.40 mg P L^{-1}).

At the mainstem station (Bell Shoals), mean monthly OP concentrations were similar during 1991– 1999 (0.30 mg P L^{-1}; 17% of total P) and 2000–2009 (0.29 mg P L^{-1}; 19% of total P) (Fig. 4-2C). At two developed (North Prong and Turkey Creek) and one undeveloped (South Prong) sub-basin, the concentrations of OP were slightly greater (0.09–0.6 mg P L^{-1}) during 1991–1999 than 2000–2009 (0.1–0.3 mg P L^{-1}). Among the sub-basins, mean OP concentrations were slightly greater in developed (0.21–0.34 mg P L^{-1}) than undeveloped sub-basins (0.12–0.15 mg P L^{-1}). The greatest concentrations of other P forms were at North Prong (0.34 mg P L^{-1}) and lowest at South Prong (0.12 mg P L^{-1}) during 2000–2009.

Seasonal Variation in Phosphorus Concentrations in Streams Draining Different Sub-basins

The water quality data from 1991–2009 showed that total P concentrations in stream water were greater, but not statistically significant ($P < 0.05$) in wet than dry season at all study stations (Fig. 4-3A). At two mainstem stations, total P concentration was 40–45% greater in wet (1.26–1.88 mg P L^{-1}) than dry season (0.90–1.30 mg P L^{-1}). In developed sub-basins, the concentration of total P was 63% greater at English Creek (2.93 mg P L^{-1}) followed by 38% greater at Turkey Creek (1.04 mg P L^{-1}) and 9% greater at North Prong (3.42 mg P L^{-1}) in wet than dry season. In undeveloped sub-basins, total P concentrations were 9–20% greater in wet (0.60–0.95 mg P L^{-1}) than dry season (0.55–0.79 mg P L^{-1}).

Similar to total P, mean concentration of DRP was greater, but statistically ($P<0.05$) similar in wet and dry seasons at all the study stations (Fig. 4-3B). At two mainstem stations, the DRP concentration was 21–46% greater in wet (1.03–1.39 mg P L^{-1}) than dry season (0.71–1.14 mg P L^{-1}). Among the developed sub-basins, DRP increased by 55–60% (from 0.53–1.60 mg P L^{-1} to 0.83–2.56 mg P L^{-1}) at Turkey Creek and English Creek followed a comparatively lower increase at North Prong (from 2.68 to 2.85 mg P L^{-1}; 6%) in wet than dry season. In undeveloped sub-basins, the increase in total P concentration was ~10% (from 0.39–0.71 mg P L^{-1} to 0.42–0.79 mg P L^{-1}) in wet than dry season.

Proportion of DRP was 71–90% of total P in wet and dry seasons at all the study stations (Fig. 4-4). Among the developed sub-basins, overall proportion of DRP was greater at English Creek and North Prong (83–89% of total P) than Turkey Creek (71–79% of total P). Among the undeveloped sub-basins, the greater proportion of DRP was at South Prong (83–89% of total P) than Fishhawk Creek (71%).

Mean concentration of OP forms during dry and wet seasons were statistically (P<0.05) similar; however, the magnitude of variation was greater than total P and DRP at all the sub-basins (Fig. 4-3C). For example, other P was ~220% greater at Bell Shoals (0.49 mg P L^{-1}) and 10% greater at Alafia (0.23 mg P L^{-1}) in wet compared to dry season. Among the developed sub-basins, other P concentrations increased by 80% at English Creek (from 0.20 to 0.36 mg P L^{-1}), 26% at North Prong (from 0.45 to 0.57 mg P L^{-1}), 2% at Turkey Creek (from 0.22–0.24 mg P L^{-1}) in the wet than dry season. Among the undeveloped sub-basins, the increase in OP concentration in wet compared to dry season was 100% at South Prong (from 0.08 to 0.16 mg P L^{-1}) and 8% at Fishhawk Creek (from 0.15 to 0.17 mg P L^{-1}).

Proportion of OP to total P was similar: 11–43% in dry season and 14–44% in wet season at all sub-basins (Fig. 4-4). However, at two mainstem stations, proportion of OP was greater in wet (22–40%) than dry (15–29%).

Long Term Trends in Concentrations of Flow Un-weighted Phosphorus Forms in Streams Draining Different Sub-basins

The longest data record (19 years) was available only for one mainstem station (Bell Shoals) that drains 89% of the watershed area and three other sub-basins (Fig. 4-5). The results of the Seasonal Kendall trend analysis showed a significant (P<0.002) decreasing flow un-weighted total P concentration trend (–3.8% per year; 57.6 µg P L^{-1} per year) at Bell Shoals. This decreasing trend equates to ~72% decrease in mean total P concentrations during 1991–2009. Total P concentrations trends were decreasing at North Prong (–4.8% per year; 104.2 µg P L^{-1} per year; P<0.001) and South Prong (–2.2% per year; 14.4 µg P L^{-1} per year; P< 0.03). In contrast to these sub-basins, Turkey Creek showed non-significant (P<0.29) total P concentrations trend during 1991–2009. Among the stations with 10-years of data, English Creek showed a significant decreasing total P trends (–36.5% per year; P< 0.008).

Similar to the Seasonal Kendall trend analysis, GLIMMIX model showed a significant (*P* <0.001) overall decreasing total P trend at Bell Shoals (–0.9% per year) during 1991–2009 (Fig. 4-5). At Turkey Creek, total P showed an increasing (*P*< 0.001) trend (+1.1% per year). In contrast to Turkey Creek, other two sub-basins with 19-years data record showed significant (*P* <0.001) but with lower magnitude decreasing total P concentration trends (–0.3 and –1.1% per year). The total P trends at two stations with 10-years of data record were decreasing (from –1.09 to –1.11% per year).

Seasonal Kendall trend analysis showed a decreasing DRP concentration trend (–4.4% per year; *P*<0.003) during 1991–2009 (Fig. 4-6). Among the sub-basins with 19-years of data record, DRP concentration trends showed a non significant increase at Turkey Creek (+0.5% per year; *P*<0.55) compared to a significant decreasing DRP trends at North Prong (–4.2% per year; *P*<0.002) and South Prong (–2.3% per year; P<0.09). The stations with 10-years of data record showed decreasing DRP concentration trends at Alafia (–5.6% per year; P<0.37) and English Creek (–34.3% per year; P<0.009) during 1999–2009 (Fig. 4-6).

GLIMMIX model showed a significant (P<0.001) decreasing DRP concentration trend (–1.14% per year; P< 0.001) at Bell Shoals (Table 4-6). Turkey Creek had increasing DRP concentrations trend (+0.99% per year; P<0.0001) as compared to decreasing trends at North Prong (–1.03% per year; P<0.001) and South Prong (–0.98% per year; P< 0.03). During 1999–2009, decreasing DRP trends were found at English Creek (–1.23% per year; P<0.001) and Alafia (–0.89% per year; P<0.018).

Both the Seasonal Kendall and GLIMMIX procedures showed non-significant trends for OP concentration at all sub-basins (Fig. 4-7). However, other P concentration trends were decreasing at Bell Shoals (from –1.06 to –1.60% per year) during 1991–2009.

Long Term Trends in Flow Weighted Concentrations at Mainstem Station

At the mainstem station that drains 89% of the Alafia River Watershed showed a significant (P< 0.041) decreasing total P concentration trend (–1.14% per year) during 1991–2009 (Table 4-2). Mean total P concentration at the mainstem station was greater during 1991–1999 (1.76 mg P L^{-1}) and 2000–2009 (1.24 mg P L^{-1}) thereby reflecting the decreasing total P concentration trends in terms of actual concentrations. Similarly, DRP showed significant (P< 0.016) decreasing trend (–1.16% per year) during 1991–2009 (Table 4-2). In contrast to total P and DRP, the flow weighted concentration trends were insignificant in OP forms (P<0.561) at Bell Shoals.

Long Term Trends in Phosphorus Loads at Mainstem Station

At mainstem station (Bell Shoals), total P loads were not significant during 1991–2009 (Table 4-2). The non significant trends in the P loads during wet and dry seasons could be due to greater variations in P loads.

Discussion

Land Use Impacts on Phosphorus Concentrations in Streams

During 2000–2009, at two mainstem stations (Alafia and Bell Shoals), total P concentrations were greater (1.02–1.76 mg P L^{-1}) than the EPA's proposed numeric total P value of 0.739 mg P L^{-1} for rivers in the Tampa Bay (EPA, 2010). In our study, total P concentrations were an order of magnitude greater than total P in Miller Creek Watersheds in Kansas, US (0.008–0.22 mg P L^{-1}, mean= 0.031 mg P L^{-1}) reported by Dodds and Oakes (2006). Concentrations of total P in our study were also greater than corn-soybean dominated (>60%) watersheds of Indiana, USA (0.13–0.23 mg P L^{-1}) (Vidon et al., 2008). It is important to note that the Alafia River flows over a geologic P rich formation (fluorapatite) that is commercially mined

for P (Lane, 1994). As a result, P concentration is comparatively higher in Alafia River than other studies conducted across US.

Mean monthly concentrations of total P were greater in two developed sub-basins (North Prong and English Creek) than other sub-basins (Fig. 4-2). This could be attributed to active phosphate mining in North Prong (39% mined land use) and small animal feeding operations in English Creek may have elevated the P concentrations in stream waters (NPDES, 2009). In addition, a wastewater treatment plant discharges 0.35 m^3 sec^{-1} of wastewater with mean total P concentration of 3.1 mg P L^{-1} in the North Prong. In our study, total P concentrations were not significantly ($P<0.05$) correlated with urban, agricultural, forest, and pasture land uses thereby indicating that P losses are not significantly affected by land uses in the Alafia River Watershed (Fig. 4-8, 4-9). Negative (r= –0.47: $P>0.05$) correlations between total P and pasture land uses might be due to the fact that pastures may act as a potential buffer to reduce the transport of P from watersheds to streams (Abelho, 2001; Wahl et al., 1997; Zaimes et al., 2008). On the other hand, slightly positive but not significant correlation between total P and urban land use (r= +0.33) may be due to greater impervious areas which increase the runoff generation to facilitate the transport of P from the watersheds (Arnold and Gibbons, 1996; Lee and Heaney, 2003; Paul and Meyer, 2001). It appears that the P concentration in the streams of the Alafia River Watershed is controlled by the geology and presence of active mined land use along with point source input from domestic and industrial (phosphate mining) wastewater. In our study, lower concentrations of total P at South Prong (66% mined land use) may be due to the fact that most of the mined lands discharge wastewaters to the sub-basin only during extremely high flow events and therefore is not impacted with mining activities.

Seasonal Impact on Phosphorus Concentrations in Streams

In our study, the concentrations of P forms were greater but not significant ($P < 0.05$) in wet than dry season at all the sub-basins (Fig. 4-3). The increase in concentrations of P forms in wet season was not significant due to greater variations in P concentrations. However, higher concentrations of P forms in the wet season represent the influence of non-point sources on P pollution in the Alafia River Watershed. Previous studies have reported greater losses of P during high flow conditions. For instance, in high fertilizer inputs corn-soybean dominated watersheds of the Midwest, US, Royer et al. (2006) reported that >80% of the P losses occurred during the extreme discharges (>90% percentile flow). Similarly, in Indian River Lagoon, Florida, due to application of fertilizers to agricultural crops in wet season the concentrations of both DRP and total P were two times greater in wet than dry season (Qian et al., 2007). Research has indicated that most solute losses occur when large quantities of solutes are present in the landscape coupled with increased flows (Boyer et al., 1997; Verseveld et al., 2009). Although mechanisms controlling the temporal pattern in P concentrations were not directly investigated, it seems probable that during the dry season the dissolution and desorption of P occurs in geologically P rich Alafia River Watershed which is subsequently flushed with increasing discharge in wet season (Chen and Driscoll, 2009; Wetzel, 2001). Another probable reason for greater concentration of P forms could be the release of P due to suspension of the stream sediments with the high flow events during the wet season (Svendsen et al., 1995).

In our study, the concentrations of other P forms were greater in wet than dry season; however, the proportions of DRP and other P forms remained similar during both wet and dry seasons (Fig. 4-4). This contradicts previous studies which reported the lower proportion of DRP in wet season (Ellison and Brett, 2006; Pacini and Gachter, 1999). In general, streams are characterized by higher proportions of DRP in dry season when the sediment transport capacity

is low as fine bed sediments are the primary source of PP and the proportions of PP increase with the transport of greater particulates into the streams during high flow conditions in wet season (Ellison and Brett, 2006; Pacini and Gachter, 1999). Similar proportions of DRP and other P forms during dry and wet seasons in our study suggests that desorption of P from the soil particles and slow dissolution of P minerals during dry season is the dominant source of P which flushed during wet season.

Long Term Trends in Concentration of Phosphorus Forms in Stream Waters

The Seasonal Kendall and GLIMMIX procedures showed similar trends (positive or negative), though with different magnitude of change (slope %) (Fig. 4-5; 4-6; 4-7). These differences in trend slopes appear to be associated with the conceptual differences in the way of calculating the slopes in both the methods. For example, Seasonal Kendall compares the change in concentrations of nutrients with time (slope) for each point and the median slope is calculated as a summary statistic describing the magnitude of the trend (Johnson et al., 2009; Qian et al., 2007). On the other hand, GLIMMIX procedure fits the linear lines through the data and slope is the rate of change in concentration with time at any of two points (SAS, 2008). Therefore, the differences in the magnitude of slopes appear in the trend analysis in two methods. In general, Kendall trend analysis determines the trends at a single location. However, GLIMMIX procedure can be used to compare the mean concentrations at multiple locations as well as has the ability to include many parameters such as stream discharge, seasonal variation, distance of the mainstem, and location of the station etc (Goodrich et al., 2009). In this study, GLIMMIX procedure has shown the significant variations in mean and seasonal variations in P concentrations at different stations.

In general, flow weighted concentration trends represent the changes due to anthropogenic activities since the natural changes due to variations in flow are minimized. On the other hand,

flow un-weighted concentrations trends reflect the net effects of all natural and anthropogenic influences on concentration, allowing for the assessment of nutrient concentrations in streams relative to water quality standards of Environmental Protection Agency and the condition of aquatic communities (Sprague and Lorenz, 2009; Johnson et al., 2009). In our study, the flow weighted and flow un-weighted concentrations showed significantly decreasing trends at Bell Shoals during 1991–2009. This has suggested that the anthropogenic activities were responsible for decreasing P trends in the Alafia River Watershed. Similar to the Alafia River Watershed, the controls on P losses from watersheds have been documented in 50% rivers in the US in last 2–3 decades (Alexander and Smith, 2006). For instance, in Minnesota River, US, Johnson et al., (2009) using Seasonal Kendall trend analysis reported the decreasing trends of total P (–2.0% per year) and DRP (–1.83% per year) during 1976–2003. They attributed the decrease in P concentrations trends to the conservation programs such as plantation of native grasses, buffer strips, wetland restoration, and reduction in agricultural activities near the streams. Similarly, in the Everglades Agricultural Area, FL, Daroub et al. (2009) reported decreasing total P concentration trends due to implementation of agricultural BMP's during 1992–2002. In contrast to these watersheds, the Alafia River Watershed has P rich geology and therefore is commercially mined for P. The discharges of P rich wastewater from the mining operations have been reduced as a result of greater regulations in the watershed (NPDES, 2009). Further, the mined land uses have been reclaimed in most of the sub-basins during 1991–2009 resulting in decreased losses of P from the mined lands.

In the Alafia River Watershed, population has grown from 0.83 million in 1990 to 0.99 million in 2000 and 1.20 million in 2009 (US Census Bureau, 2010). This represents 19.8% increase during 1990–2000 and 19.7% during 2000–2009. The population growth has resulted in

the land use changes in the watershed. For example, the urban land use (residential and built up) has increased by 8% (from 12 to 20%) of the watershed during 1990–2007 (SWFWMD, 2007). This is coupled with a decrease of 5% in forests (from 23 to 19%) and 8% decrease in pastures (from 19 to 11%) while agricultural land use remained similar (8%) during the study period. The decreasing total P and DRP concentrations trends suggest that the land use change has not resulted in increasing P concentrations in the Alafia River Watershed. This contradicts the previous studies which have suggested the greater losses of P with urbanization (Brett et al., 2005; Ellison and Brett, 2006). In our study watershed, the constructions of mandatory urban storm water retention ponds is an important feature which might have played an important role in P removal through burial of P in retention ponds sediments (Alexander et al., 2000; Bosch, 2008; Evans et al., 2004). Further, increased regulations on the discharges of P from the wastewaters and mining activities might have masked the effect of urbanization (Alexander and Smith, 2006).

Summary

The mainstem stations of the Alafia River Water (Alafia and Bell Shoals) had greater mean total P concentrations (1.01–1.76 mg P L^{-1}) than EPA's proposed numeric total P value of 0.739 mg P $L^{-1}$for the region. Greater total P concentrations at two developed sub-basins (North Prong and English Creek: 2.2–2.5 mg P L^{-1}) may be due to P rich geology as well the discharge of P rich wastewater in these sub-basins. Of total P, DRP was dominant (70–90% of total P) than other P forms (10–30% of total P) probably because of dissolution of P rich minerals in the watershed. Greater concentrations of P forms in wet than dry season may be due to flushing of P accumulated due to dissolution of P minerals. Long-term trend analysis showed decreasing flow un-weighted and flow weighted concentrations of total P and DRP thereby suggesting that the P abatement programs such as increased regulations on the wastewaters facilities and reclamation of mined lands might have resulted in reducing concentrations of P in the Alafia River

Watershed. Despite the decreasing P trends, the concentration of total P was still greater than the EPA's proposed numeric nutrient criteria (0.739 mg P L^{-1}) for the region. Therefore, the reduction in P loss from mined lands and wastewater discharges in four sub-basins (North Prong, English Creek, Turkey Creek, and South Prong) may result in reducing total P concentrations in the Alafia River Watershed.

Table 4-1. Station characteristics of the Alafia River Watershed

Sub-basin	Station	Sampling location		Drainage area		Land Use in 2007					
		Lat	Long	km^2	%	Residential	Built up	Agricultural	Pasture	Forest	Mined
					Mainstem Stations						
Alafia	2301718	27.87	–82.32	1072	99	17	3	8	11	18	32
Bell Shoals	2301638	27.86	–82.26	974	89	16	3	8	12	18	33
					Developed						
English Creek	-†	27.93	–82.06	99	9	21	14	19	23	25	3
Turkey Creek	-†	27.91	–82.18	128	13	20	3	24	16	12	0
North Prong	2301000	27.86	–82.13	350	32	18	6	4	5	16	39
					Undeveloped						
South Prong	2301300	27.86	–82.13	277	26	3	1	4	9	15	66
Fishhawk Creek	†	27.85	–82.24	70.6	7	11	3	14	23	32	0

-† USGS station not present

Table 4-2. Long term trends in flow weighted and loads of P forms at Bell Shoals

Parameter	**D**ata	Flow weighted concentrations			Loads		
		Trend	Slope (%)	p value	Trend	Slope	p value
Total Phosphorus	1991–2009	Decreasing	–1.14	0.041	No trend	–	0.535
Dissolved Reactive P	1991–2009	Decreasing	–1.16	0.016	–	–	–
Other P	1991–2009	No trend	–	0.561	–	–	–

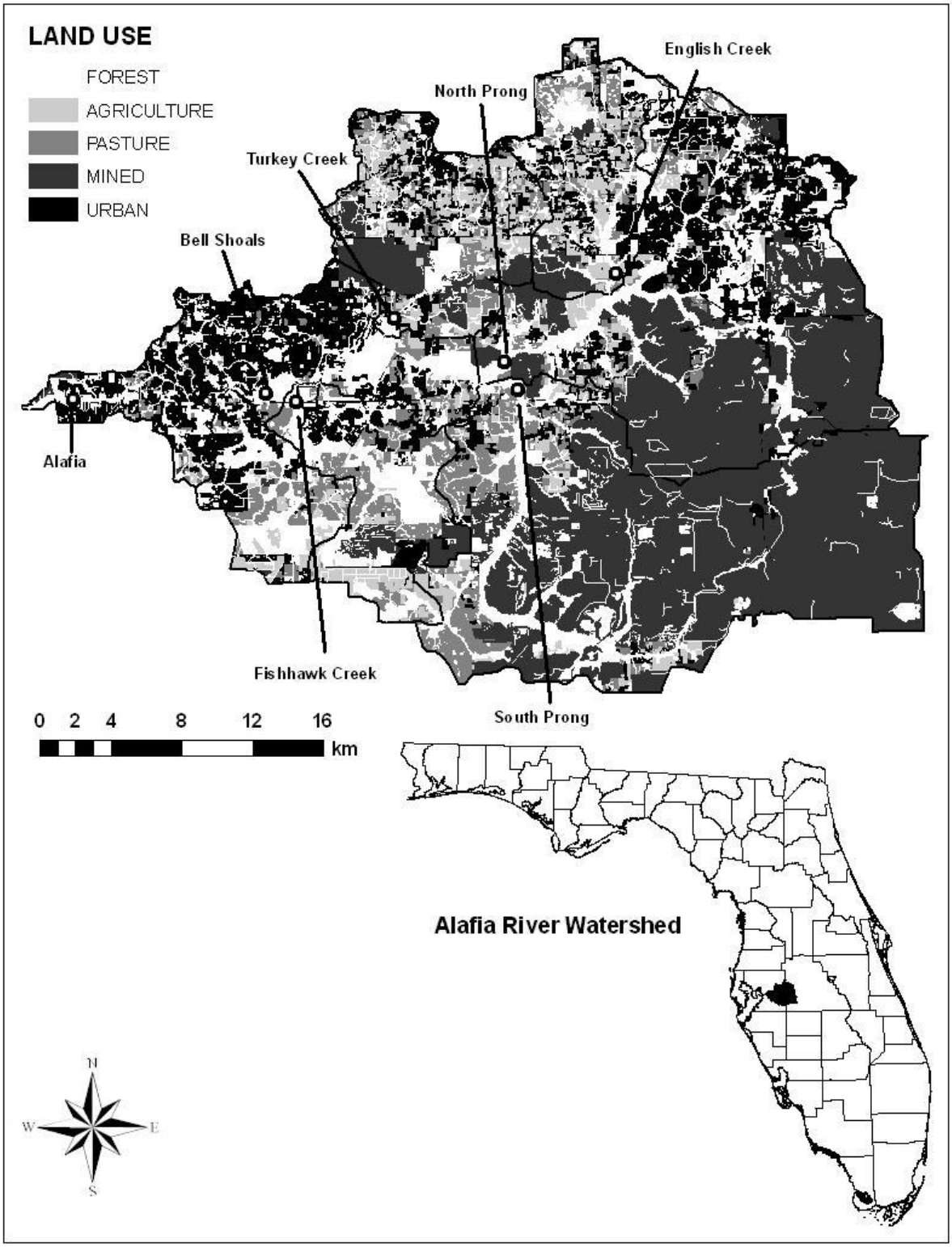

Figure 4-1. Location map of the Alafia River Watershed.

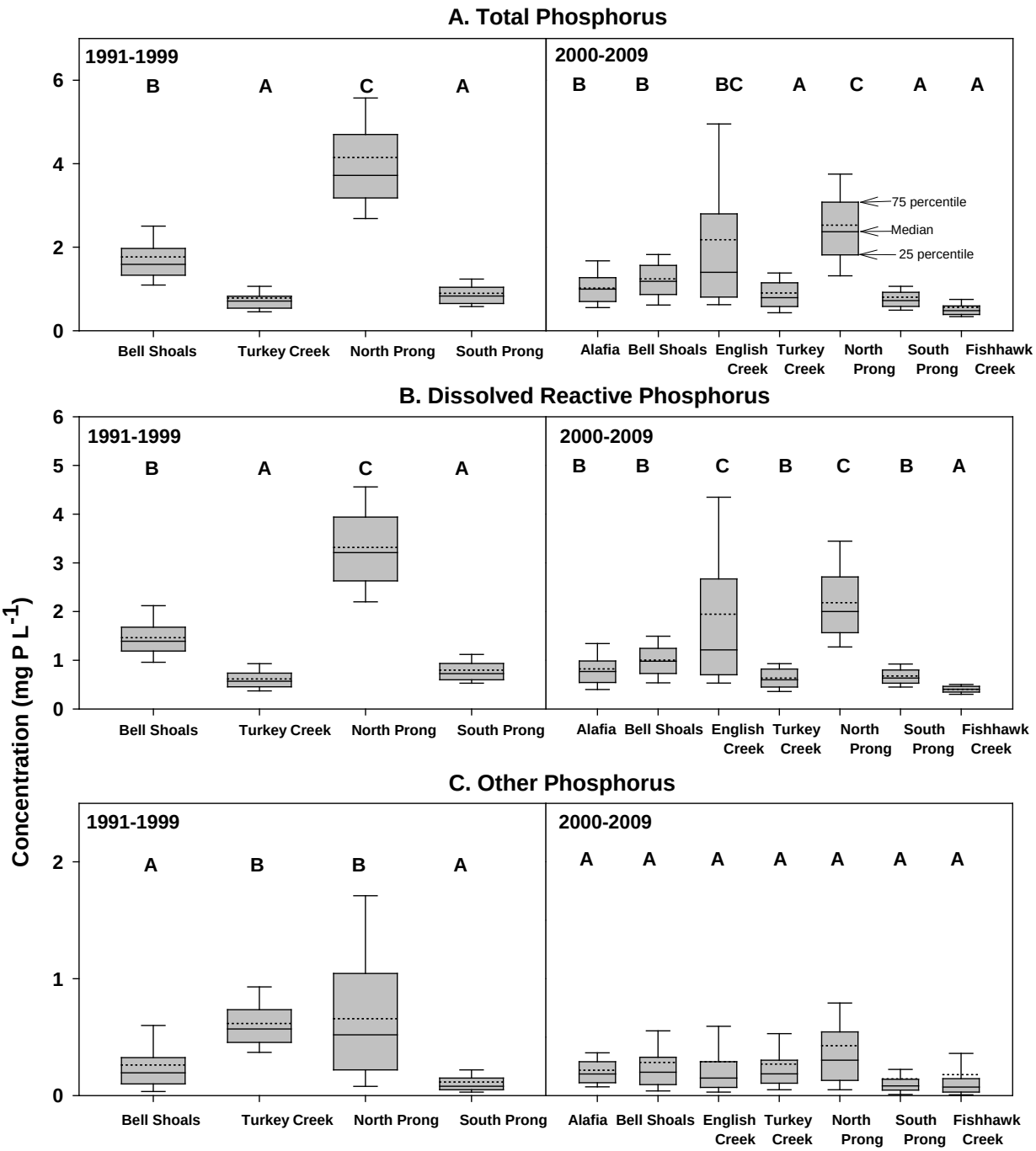

Figure 4-2. Summary of mean monthly concentrations of total, dissolved reactive, and other phosphorus forms during 1991–2009 in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek). Values indicated by different letters are significantly different according to GLIMMIX procedure at $P < 0.05$. N in each sub-basin indicates number of months/observations.

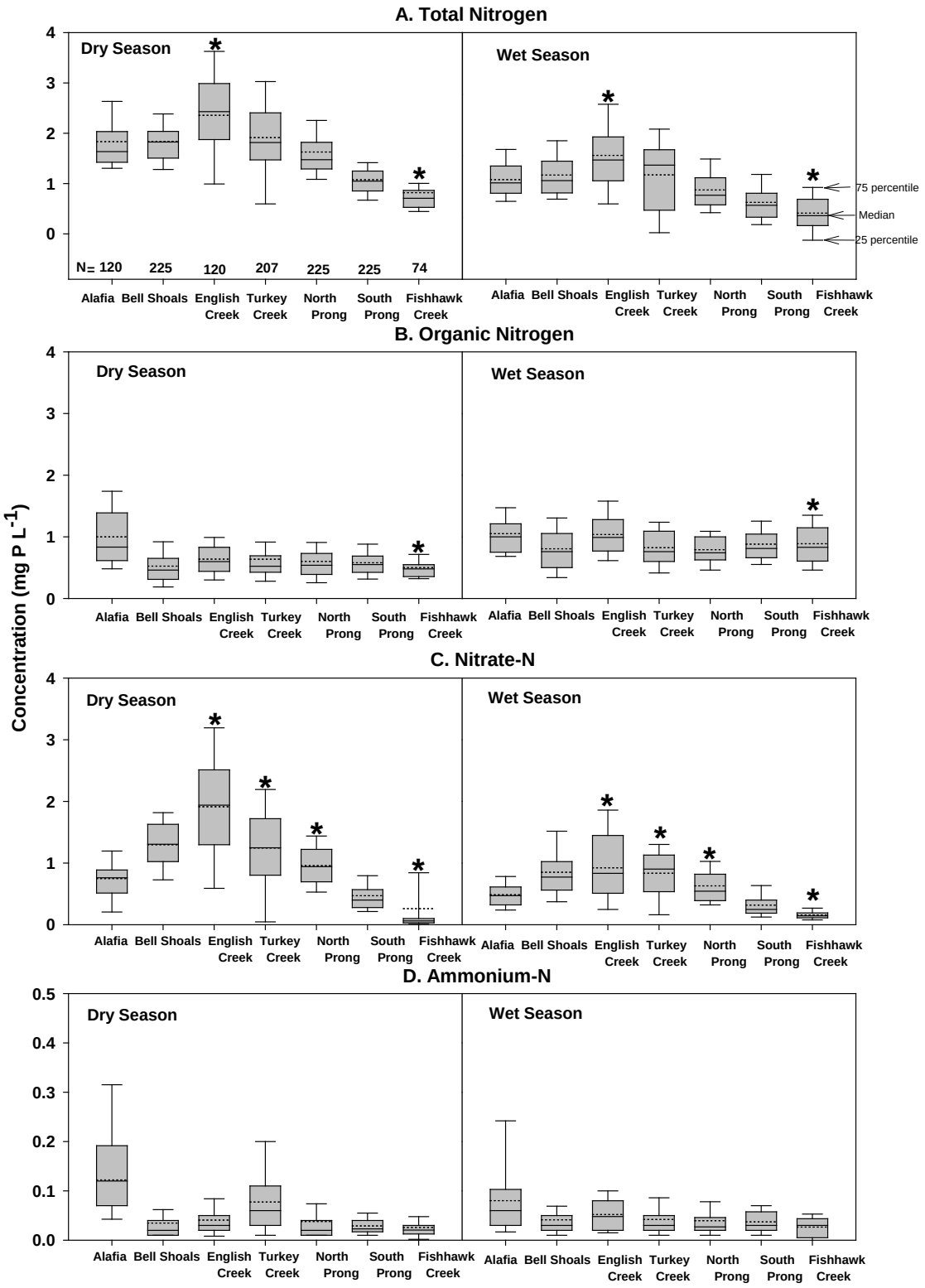

Figure 4-3. Seasonal variation in mean monthly concentration of phosphorus forms during 1991–2009. Values indicated by different letters are significantly different according to GLIMMIX procedure at P< 0.05. Dotted line represents the mean value.

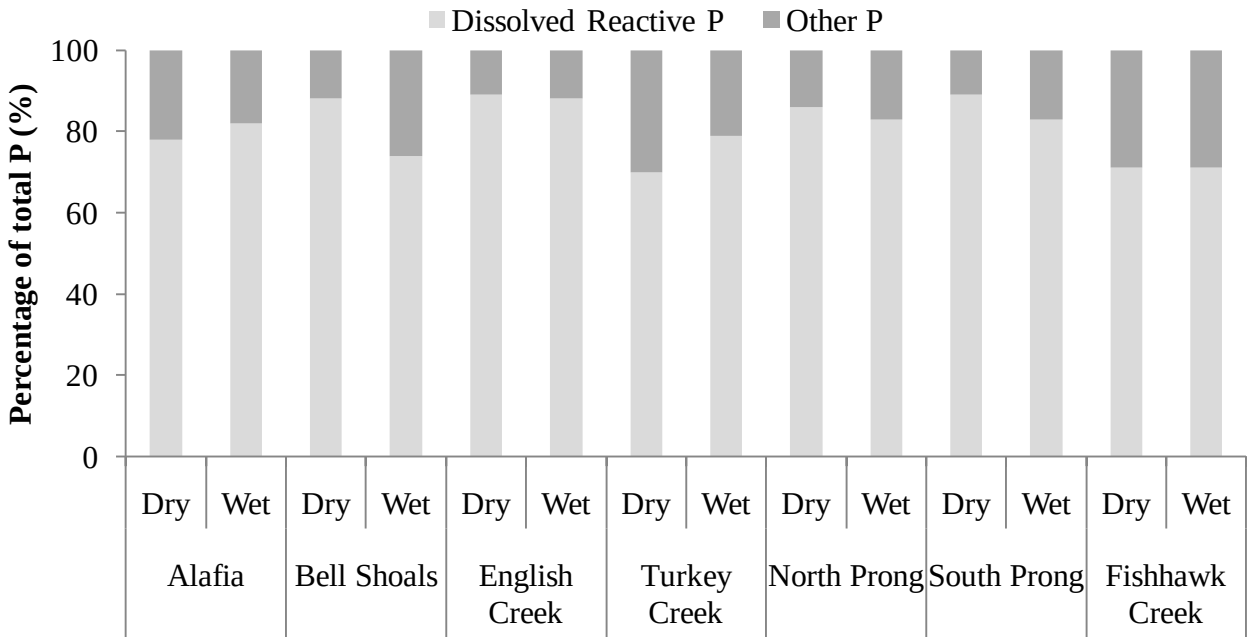

Figure 4-4. Seasonal variation in contribution of organic, nitrate, and ammonium nitrogen to total nitrogen during 1991–2009.

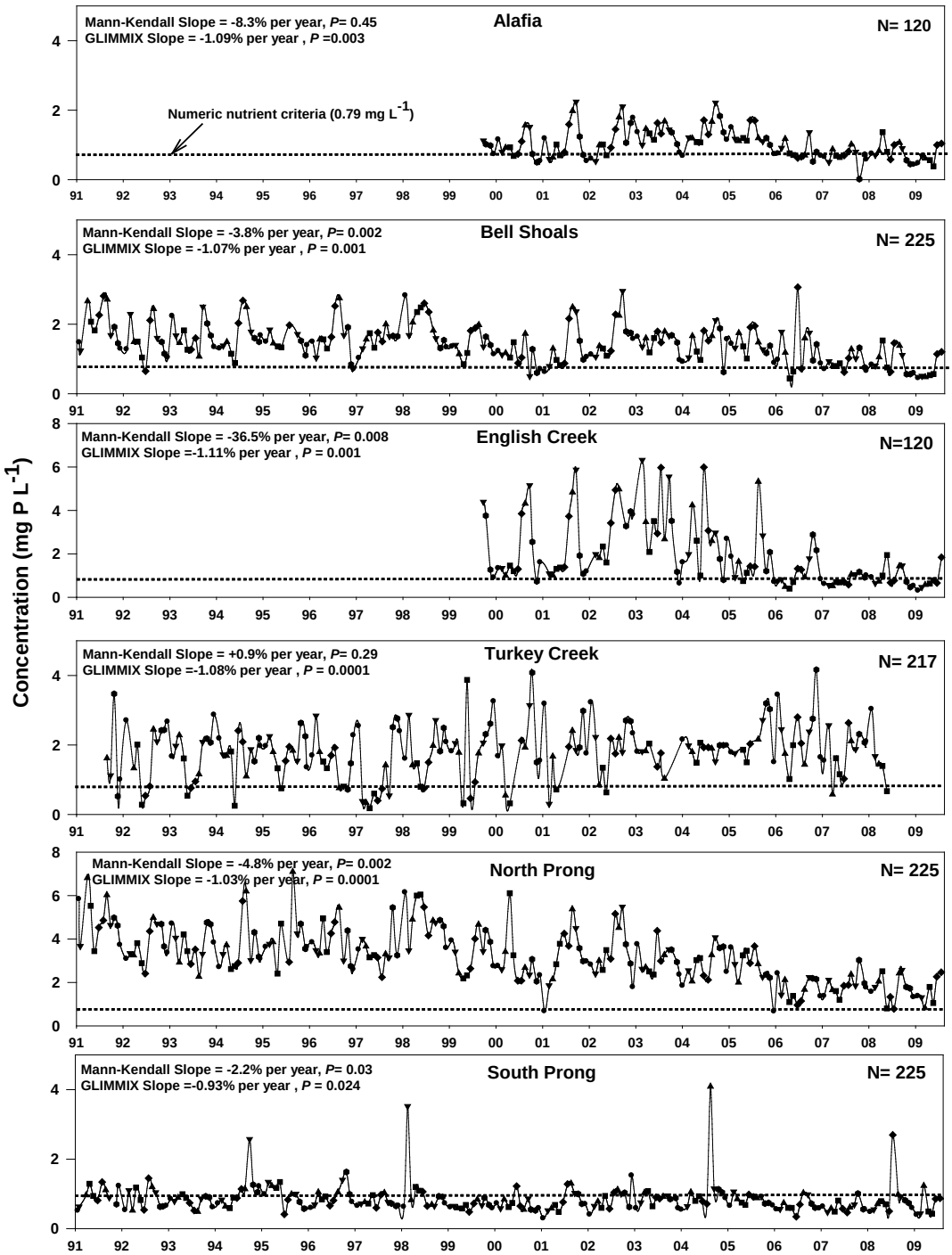

Figure 4-5. Long-term (1991–2009) trends in mean monthly total P concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed. The dotted line indicates the proposed numeric nutrient (0.79 mg L^{-1}) criteria for the region (EPA, 2010).

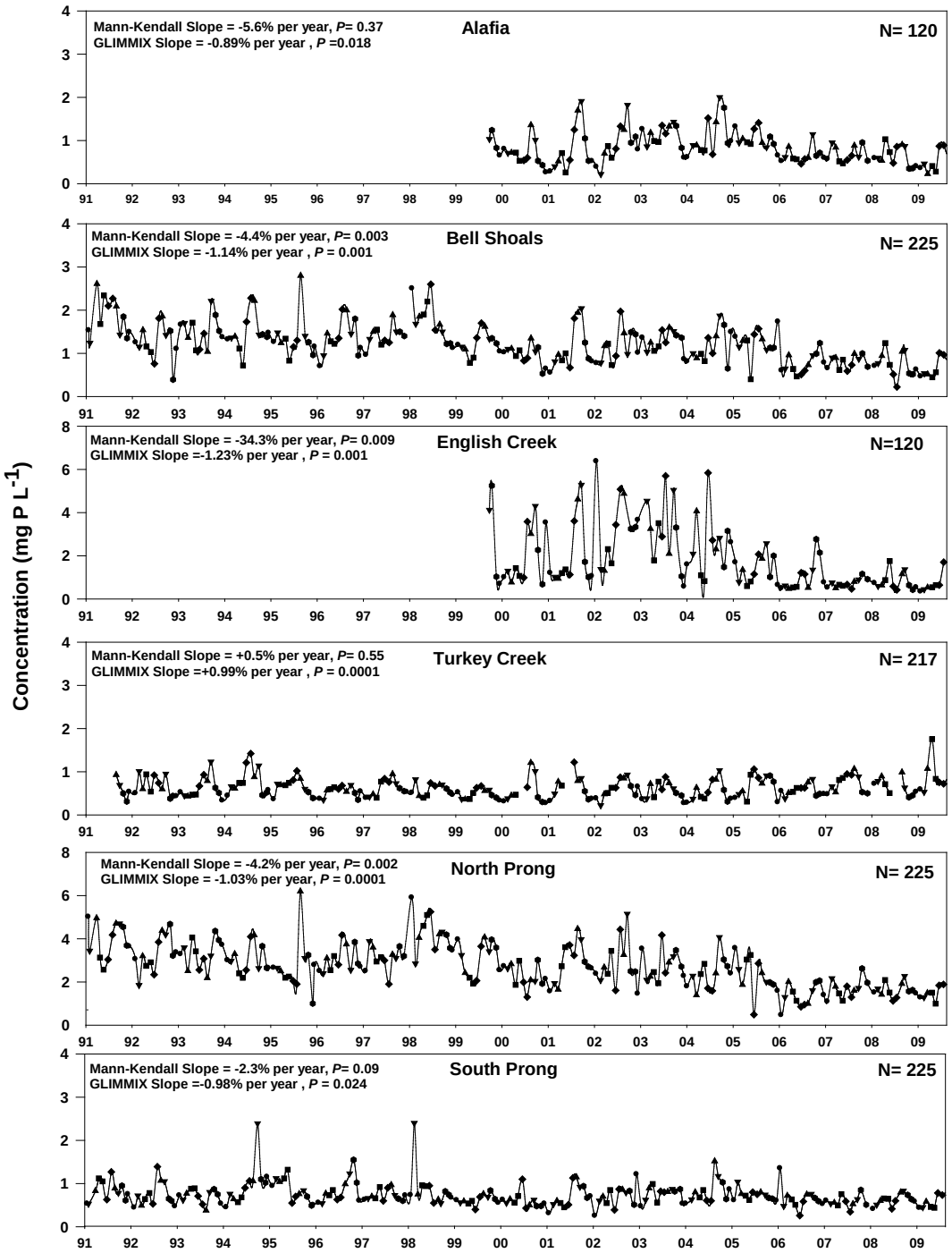

Figure 4-6. Long-term (1991–2009) trends in mean monthly dissolved reactive P concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed.

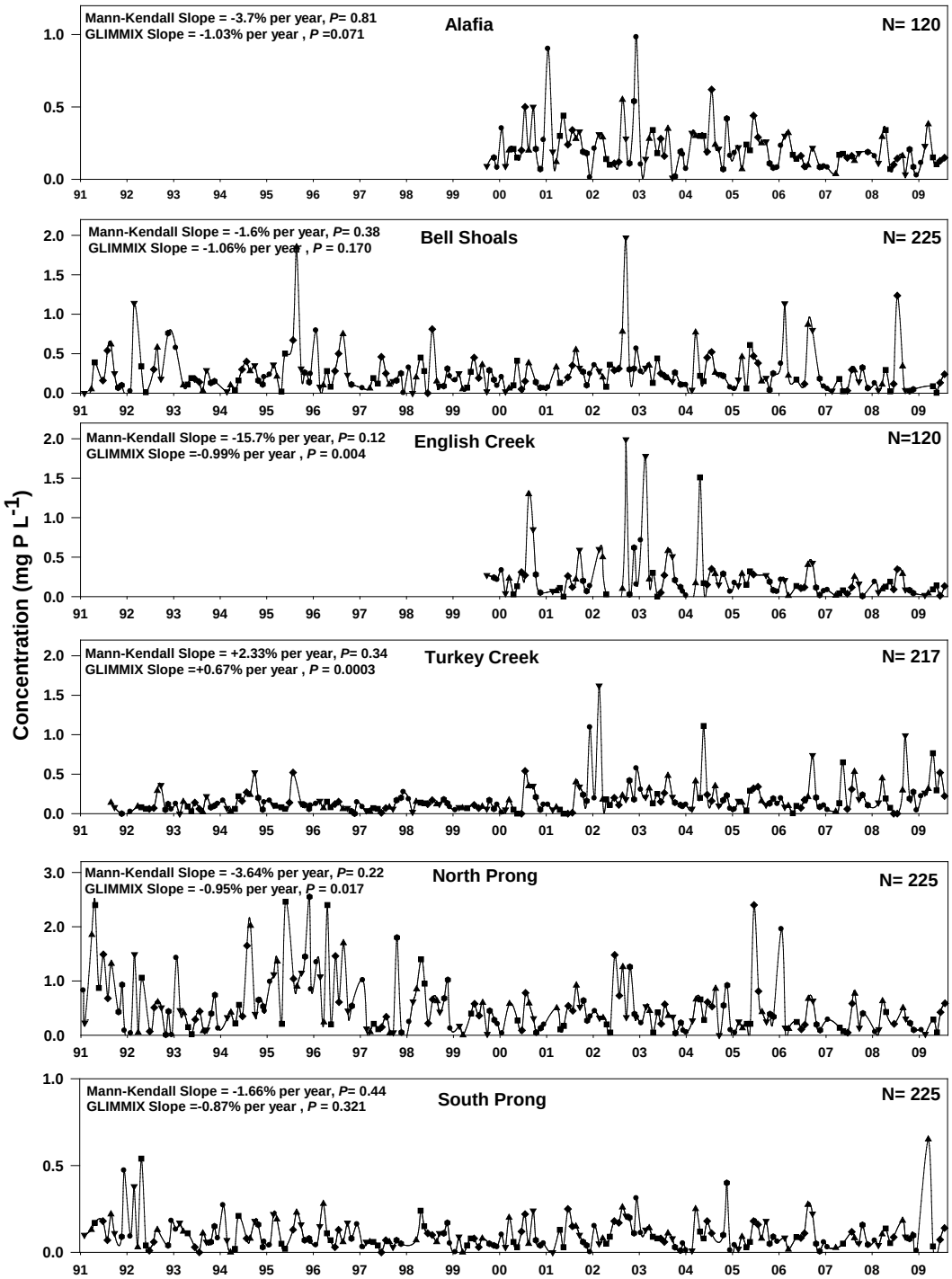

Figure 4-7. Long-term (1991–2009) trends in mean monthly other phosphorus forms concentrations in mainstem (Alafia and Bell Shoals), developed (English Creek, Turkey Creek, and North Prong), and undeveloped (South Prong and Fishhawk Creek) sub-basins of the Alafia River Watershed.

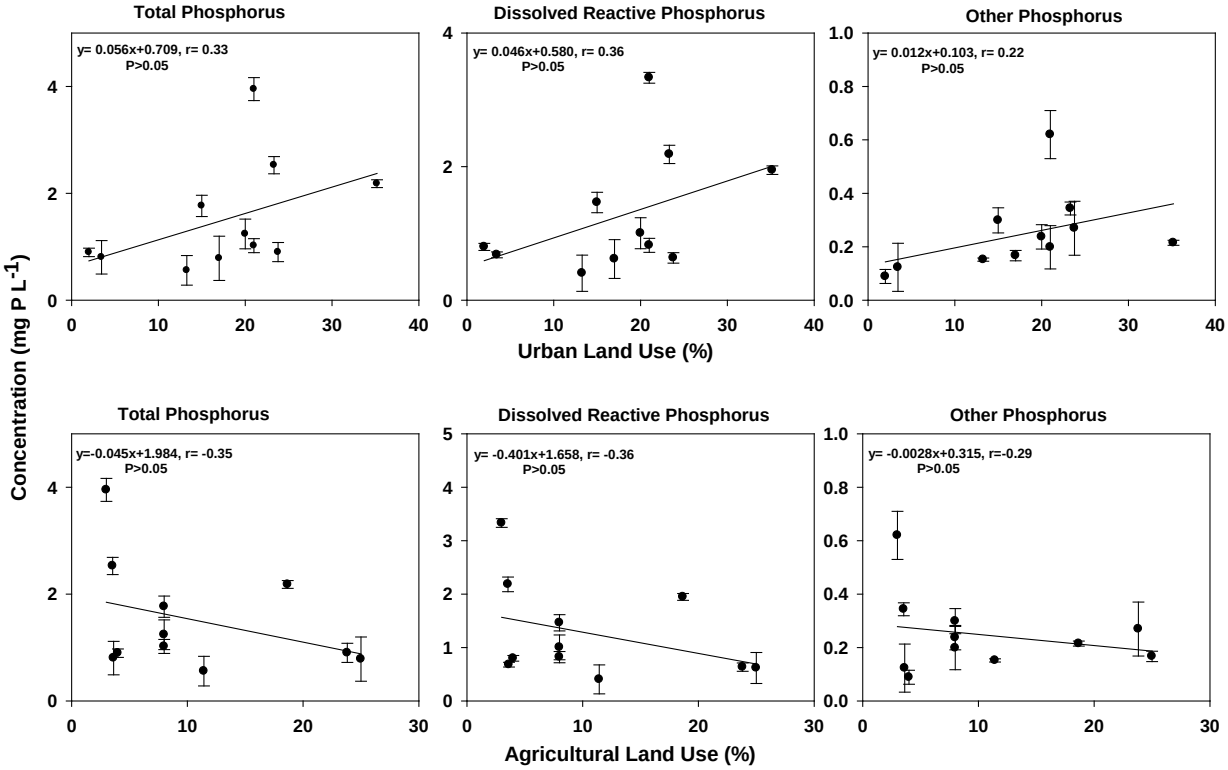

Figure 4-8. Relationship between percent urban and agricultural land use and phosphorus forms in different sub-basins (* significantly correlated at P< 0.05). The mean monthly data of 2001–2009 was correlated with the land use during 2007.

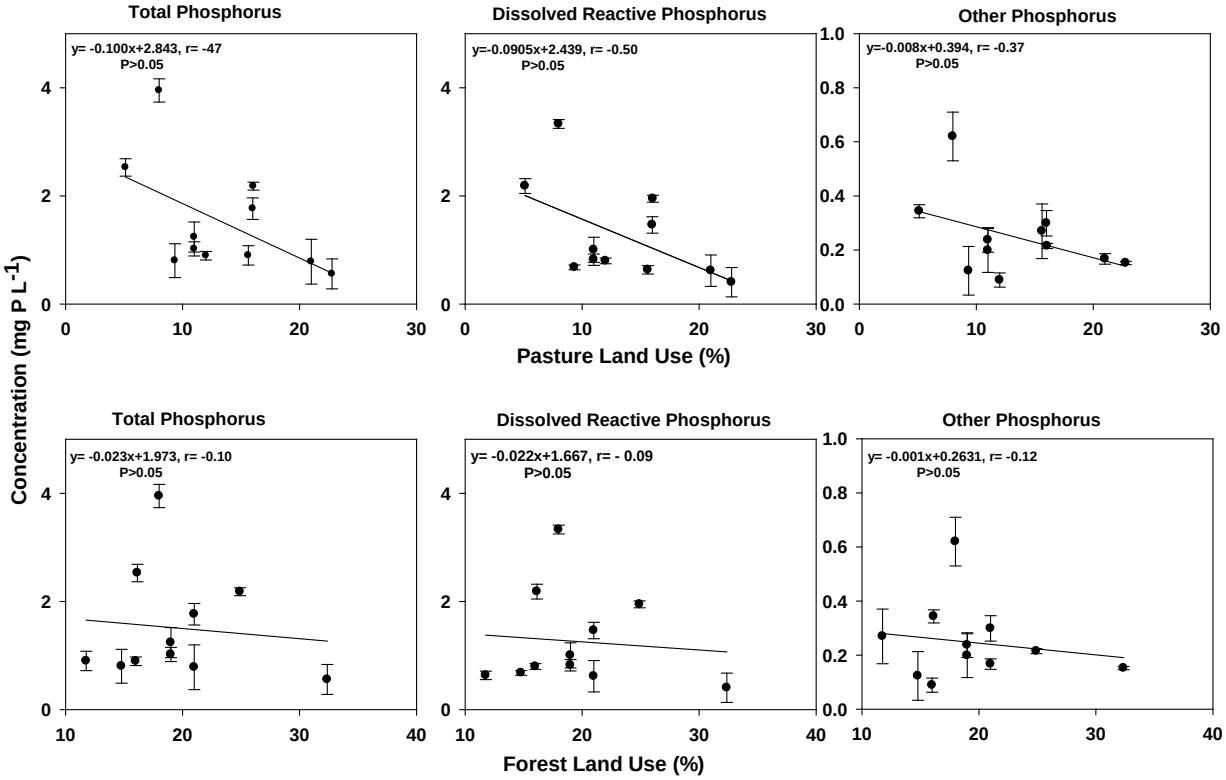

Figure. 4-9. Relationship between pasture and forest land use and phosphorus forms in streams draining different sub-basins (* significantly correlated at P< 0.05).

CHAPTER 5
SUMMARY, CONCLUSIONS, AND RECOMMENDATION

The anthropogenic activities such as urbanization and agriculture have increased concentrations of nitrogen (N) and phosphorus (P) in lakes, rivers, reservoirs, and estuaries resulting in eutrophication of water bodies. In the US, nearly 60% of 138 estuaries exhibit moderate to severe eutrophic conditions and >90% rivers have either N or P concentrations greater than the respective reference levels. In general, anthropogenic influences (urban and agricultural) in watersheds result in greater nutrient inputs such as fertilizer application to crops, urban lawns, and septic tanks which may lead to greater losses of nutrients to streams. Another consequence of changes in land use, primarily in urbanizing watersheds, is the increase in impervious areas such as rooftops, roadways, parking lots, sidewalks, and driveways. These impervious areas increase runoff and minimize the biotic uptake processes that immobilize nutrients in the forest canopy, litter, soils, and organic matter and thereby result in greater losses of nutrients. Florida is one of the rapidly developing states in the US and has serious water quality problems with nutrients especially eutrophication of coastal waters. Therefore, it is important to assess the impact of anthropogenic activities on water quality in waterbodies of Florida. Very little is known about N and P transport in urban watersheds in Florida, which is dominated by sandy soils, high ground water table, P rich geology, and altered hydrology due to construction of stormwater retention ponds to avoid flooding.

In this study, we used monthly collected data (5–19 years for various sites) of stream water N and P forms for seven sub-basins (19–350 km^2) of the Alafia River Watershed (total drainage area: 1085 km^2). In the Hillsborough County where this watershed is located, population has increased from 0.83 million in 1990 to 0.99 million in 2000 and 1.20 million in 2009. This increase in population has resulted in significant changes in land uses in the

watershed. We used, Florida Land Use and Cover Classification Codes (FLUCCCS) at level IV and grouped land uses into six main categories: residential, built up, agricultural, pasture, forest, and mined using land use data of three time periods (1990, 1999, and 2007). During 1990–2007, urban land use (residential and built up) in the watershed increased by 8% (from 12 to 20%) while forest decreased by 6% (from 25 to 19%) and pasture decreased by 8% (from 19 to 11%). The agricultural land use remained similar at 8% during 1990–2007. Based on the urban land use of 2007, we classified the sub-basins into: (1) three developed (18–24% residential; 1–14% built up; 4–24% agricultural; 0–39% mined) and (2) two undeveloped (3–11% residential; 1–3% built up; 4–14% agricultural; 0–66% mined). In addition, two mainstem stations draining 89–99% of the watershed had 16–17% residential, 3% built up, 8% agricultural, and 32–34% mined land uses in 2007.

Long term monthly collected data showed that at mainstem stations (Alafia and Bell Shoals), total N concentrations of 1.77–1.91 mg L^{-1} were similar to EPAs proposed numeric total N value of 1.79 mg L^{-1} for the region (EPA, 2010). Total N concentrations were significantly ($P<0.05$) correlated with percent urban land use ($r=0.83$) but not with agricultural, pasture, mined, and forest land uses ($r<0.50$) suggesting that urbanization has increased N concentrations in stream waters. This is further reflected in significant ($P<0.05$) total N in three developed (1.67–2.43 mg L^{-1}) than two undeveloped (0.84–1.21 mg L^{-1}) sub-basins during 2000–2009. Greater proportion of NO_3-N was observed in developed (53–68% of total N) than undeveloped sub-basins (25–30% of total N). Concentration of NO_3-N was lower in wet than dry season due to greater biotic uptake and greater denitrification of NO_3-N due to higher temperature in wet season. In contrast, ON concentrations were greater in wet than dry season probably due to the greater transport of organic materials (leaves, grass) with more runoff. During 1991–2009,

concentrations showed increasing trends at the mainstem station thereby indicating that urbanization has increased total N in the streams. Interestingly, the increased total N concentration trends were primarily due to increases in ON rather than NO_3-N. This suggest processing of NO_3-N in our watershed and likely conversion to ON in stormwater retention ponds. In addition, greater runoff generation in urban land uses may enhance the transport of organic materials such as composts, grass cuttings from urban lawns, deciduous leaves fallen on the ground. As these are rich sources of ON, decomposition or leaching of N may have resulted in increased ON concentrations in the watershed. The increased ON concentration trends in this urbanizing watershed has raised two important questions (1) Is the increase in ON concentration due to greater ON sources in urban land uses? and (2) Is the ON increase a product of microbial transformations of NO_3-N into ON?. Further studies on the source characterization of the ON can help in devising the accurate BMP's to control N pollution in the Alafia River Watershed.

Total P concentrations ranged from 1.01 to 1.23 mg P L^{-1} and were much greater than EPA's proposed numeric total P value of 0.739 mg P L^{-1} for the region. Of total P, dissolved reactive P (DRP) was dominant (70–90% of total P) than other P (10–30% of total P) in both developed and undeveloped sub-basins. None of the P forms were significantly ($P < 0.05$) correlated with urban, agricultural, forest, and pasture land use ($r<0.50$) indicating that the P concentrations are not controlled by these land uses in the Alafia River Watershed. Two developed sub-basins had significantly greater total P concentrations (North Prong and English Creek: 2.18–2.53 mg P L^{-1}) probably due to P rich geology, active mined lands, and discharges of P rich wastewaters. In all the developed and undeveloped sub-basins, the concentrations of P forms were greater in wet than dry season. This indicates perhaps the flushing of P from dissolution and desorption of P from soil minerals and suspension of the stream sediments with

greater runoff in wet season might have elevated P concentrations in stream waters. The decreasing flow weighted and flow un-weighted total P concentration trends indicated that the anthropogenic activities such as increased regulations on P discharges from mined lands and, wastewater discharges together with reclamation of mined lands were probably successful in controlling P pollution in the Alafia River Watershed.

If the EPA proposed numeric total N and P criteria for Florida streams is established, it will be increasingly difficult to maintain concentrations of total N below 1.798 mg L^{-1} and total P below 0.739 mg L^{-1} in this urban watershed, unless the mechanisms controlling N and P transport from the landscape are clearly understood and BMPs to control nutrient losses from watershed are developed and implemented. In the short-term, our results can aid in planning efforts to reduce N and P concentrations. We suggest that BMPs should be targeted to control N loss in three developed sub-basins (English Creek, Turkey Creek, and North Prong) that had total N concentrations of 1.7–2.4 mg L^{-1}as these may yield greater reductions in N concentrations at watershed scale. On the other hand, due to P rich geology and discharges from wastewaters, all developed and one undeveloped sub-basins had greater total P concentrations (0.8–2.5 mg P L^{-1}) than EPA proposed numeric value of 0.739 mg P L^{-1}. Therefore, the reduction in P loss from mined lands and wastewater discharges in four sub-basins (North Prong, English Creek, Turkey Creek, and South Prong) may result in reducing total P concentrations in stream waters.

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BIOGRAPHICAL SKETCH

Kamaljit was born in Northwest India (Punjab). The eldest of the three children, he spent earlier period of his life in Punjab. After his bachelor's at Punjab Agricultural University, India in 2005, he completed his master's in soil science and agricultural chemistry at University of Agricultural Sciences, Bangalore, India. In August 2008, he started another master's program in soil and water sciences under the supervision of Dr. Gurpal Toor at the Gulf Coast Research and Education Center-Wimauma, University of Florida. Kamaljit received his master's degree from the University of Florida in the summer 2010.