COMPARING NUTRIENT EXPORT FROM FIRST, SECOND, AND THIRD ORDER WATERSHEDS IN THE SOUTH CAROLINA ATLANTIC COASTAL PLAIN

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Abstract—Monitoring of stream water chemistry in forested watersheds provides information to environmental scientists that relate management operations to hydrologic and biogeochemical processes. We used data for the first order watershed, WS80, and second order watershed, WS79, at Santee Experimental Forest. We also used data from a third order watershed, WS78, to identify the differences in temporal changes of stream water chemistry from 2006 to 2012. Phosphate concentrations for WS80 and WS79 decreased from 2006 to 2012. Most of the nitrogen (N) component was dominated by organic N and the watershed that registered highest organic N also registered highest total N concentration. Phosphate and N concentrations for all watersheds varied with rainfall received in the area. The annual mean pH of all watersheds significantly increased with stream conductivity (p < 0.05). The differences in fluctuations of observed annual stream water nutrient concentrations for all watersheds may provide a basis for nutrient availability for aquatic responses.

INTRODUCTION

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The stream water chemistry at Santee Experimental Forest in South Carolina is routinely monitored for environmental assessment records, and data can be used by researchers to identify potential impacts of burning, land uses, and weather changes on water quality. Richter and others (1983) reported that most of the nitrogen (N) for Santee Forest is in organic form and that phosphate and potassium (K) concentrations were mostly from soil derived particulates for data collected from 1976 to 1979. Wilson and others (2006) also reported higher organic N than inorganic N when analyzing data for the periods of 1976-1981 and 1989-1994. The organic N concentration contributed most to total nitrogen (TN) of Turkey Creek (third order watershed) for 2006-2008 (Amatya and others 2009). Amatya and others (2009) also reported an inverse relationship between dissolved oxygen and stream temperature for Turkey Creek. Ammonium nitrogen and phosphate concentrations decreased with flow and the greatest portion of stream water TN concentration was organic N for the two first order watersheds in Coastal North Carolina (Amatya and others 2006, 2007). Lu and others (2005) also documented that variation in flow and rainfall lead to variation in stream nutrient concentrations. Other factors that can lead to variation in stream water chemistry of watersheds are seasonal

temperature variation, spatial and temporal variations of land use, vegetation cover and silivicultural management practices (Lu and others 2005). The fact that fertilizers are not applied to Santee Experimental Forest, nutrient concentrations are hypothesized to decrease with plant age due to increasing plant uptake and fluctuate with flow. Therefore, studying the temporal changes of N components (NH_4 -N, NO_3 -N, TKN, organic N, and inorganic N) and phosphorus (P) within each watershed and among watersheds is very important for nutrient availability and stream water quality assessment.

The data reported were collected from three watersheds: a first order watershed (WS 80), a second order watershed (WS79), and a third order watershed (WS78) of drainage areas of 160 ha, 500 ha, and 5,240 ha, respectively. WS79 is comprised of two first order watersheds, the relatively undisturbed (WS80) as a control and a treatment (WS77) that is subjected to prescribed burning, and a small area in between. The objective was to compare N and P concentrations among the first order (WS80), second order (WS79), and third order (WS78) watersheds for a period of 2006-2012. Other physical and chemical parameters compared were stream temperature, pH, specific conductance, and dissolved oxygen (DO) concentration.

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MATERIALS AND METHODS

First (WS80), Second (WS79), and Third (WS78) Order Watersheds

The site for the watersheds is located in the South Carolina coastal plain (33.15° N and 79.8° W). Established in 1968, WS80 is a mosaic of upland (70 percent) and wetland (30 percent) forests with an area of 160 ha and drains the first order streams to Turkey Creek. Soils for WS80 are classified as somewhat poorly to poorly drained (SCS 1980). Loblolly pine and hardwoods currently predominate WS 80. The elevations range from 4 to 6 m with 0 to 3 percent slope for WS80. The weather parameters reported by Harder and others (2007) included a mean annual temperature of 18.3°C and average annual precipitation of 1370 mm. Other authors have documented the site's hydrologic changes and water quality (Sun and others 2000, Amatya and others 2003, 2006, 2007). WS79 (mosaic upland (75 percent) and wetland (25 percent) forests) is a second order watershed with a drainage area of 500 ha formed by streams from two first order watersheds, WS80 (160 ha) and WS77 (155 ha). WS77 is dominated by loblolly pine and subjected to prescribed burning. The third order watershed, WS78 is a mosaic upland (90 percent) and wetland (10 percent) forest, and has a drainage area of 5240 ha. The elevation of WS78 ranges from 3.6 m at the stream gauging station to 14 m above mean sea level. WS78 soils consist of poorly drained soils of Wahee (clayey, mixed, thermic Aeric Ochraquults) and Lenoir (clayey, mixed, Thermic

Aeric Paleaquults) series (SCS 1980) and small areas of somewhat poorly and moderately well drained sandy and loamy soils. The greatest land use within the watershed is loblolly pine (*Pinus taeda* L.) and long leaf pine (*Pinus palustris*) forest. Other land uses of WS78 include forested wetland and hardwood and crop lands, roads and open areas (Amatya and others 2009). Details, uses and weather parameters measured at WS78 were documented by Amatya and others (2009). Figure 1 shows the location map for WS80, WS79, and WS78. Other details of the watersheds are posted on the website, http://cybergis. uncc.edu/santee/waterQualityPage.php.

Water Quality Monitoring and Analysis

Grab samples were collected weekly, or more frequently depending upon the storm size, and analyzed for N (NH₄-N, NO₂-N, and total N) and P (in the form of phosphate) from 2006 to 2012. Amatya and others (2007) described the details of water quality monitoring and analysis. Bottles with samples preserved were frozen until the sample analysis at the Soil Chemistry Laboratory in Charleston, South Carolina. The parameters of stream temperature, pH, specific conductance, and dissolved oxygen (DO) concentration were also determined as a function of time. Water samples at the watershed outlets were collected using an ISCO 3700 sampler. Ammonium nitrogen in water was analyzed by QuikChem[®] Method, Flow Injection Analysis Calorimetry. Nitrate-nitrite was determined by the QuikChem[®] Method 10-107-04-1, Flow Injection Analysis. Total N was determined by

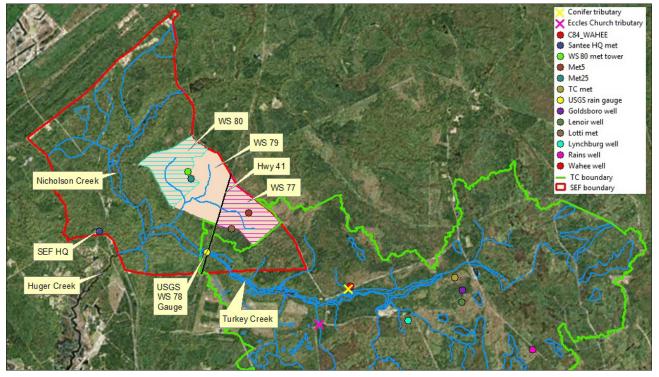


Figure 1-Location map of watersheds WS80, WS79, and WS78 (from Amatya and others 2015).

QuikChem[®] Method 10-107-04-3-B, In-Line Digestion Followed by Flow Injection Analysis). The detection limits for NH_4 -N, NO_3 -N, and total N were all 0.01 mg L⁻¹. Dissolved inorganic nitrogen (DIN) was calculated as a sum of NH_4 -N and NO_3 -N, and DON was calculated as total N minus DIN. Phosphate was determined by Micro-membrane Suppressed Ion Chromatography. Details of water quality monitoring and analysis are also posted on the website, http://cybergis.uncc.edu/santee/ waterQualityPage.php, under metadata.

RESULTS AND DISCUSSION

Temporal Changes of pH, Stream Conductivity, Dissolved Oxygen, and Temperature

Table 1 shows the annual mean and ranges for pH, stream conductivity, dissolved oxygen, and temperature. The annual mean pH followed the trend WS80>WS78>WS79 except for 2008 and 2010. WS80 registered the highest conductivity compared to WS79 and WS78 from 2006 to 2012. WS78 recorded the highest DO concentration from 2006-2012; the DO concentration trend was WS78 > WS80 > WS79. There were no significant differences in stream temperatures between watersheds (p > 0.05). A positive correlation between annual mean pH and stream conductivity (p < 0.05) for all watersheds was recorded. Annual mean stream conductivity of WS79 and WS78 significantly increased with stream temperature (p < 0.05). Annual mean dissolved oxygen significantly increased with a decrease in temperature for WS78 (p < 0.05).

We found an inverse relationship of DO concentrations with the water temperature for 2006 to 2008, with high values during the cold winter (maximum of 14.3 mg L^{-1} in January 2007) and lower values (lowest of 1.36

mg L⁻¹ in June 2006) during the hot summer months, with an average of 6.1 mg L⁻¹ for WS78 (Amatya and others 2009). The pH levels and DO concentrations for watersheds were partly attributed to natural conditions and swamp conditions by Lebo and others (2000). The interactions of parameters could be attributed to varying sizes of the watersheds, seasonal variations in flows and rainfall, variation in land uses, and vegetation growth patterns (Lu and others 2005).

Temporal Changes of Nitrogen and Phosphorus

Figures 2 to 7 show changes of annual mean N and phosphate concentrations from 2006 to 2012 for all watersheds. The decreasing concentration trend with increased rain was more pronounced with phosphate than N. The annual rain received in the area was 1264, 1041, 1521, 1458, 1380, 959, and 1117 mm in 2006, 2007, 2008, 2009, 2010, 2011, and 2012, respectively. For all watersheds, organic N was higher than inorganic N (Fig. 4 and 5). The watersheds that registered highest organic N also registered highest total N (Fig. 5 and 6). Except for 2006 and 2010, total N was highest for WS80 than WS78 and WS79. Watersheds 80 and WS78 registered a systematic decrease in phosphate concentrations from 2008 to 2012 unlike WS79. Ammonium nitrogen concentrations for WS78 were higher than NO₂-N from 2006 to 2012. Ammonium nitrogen, NO₂-N, total N, and phosphate maximum concentrations (mg L^{-1}) for WS80 were 1.07, 0.16, 2.05, and 0.58, respectively for the period 2006 to 2012. For WS79, the maximum NH₄-N, NO₃-N, total N, and phosphate concentrations (mg L⁻¹) recorded were 1.47, 0.05, 2.80, and 0.07, respectively. The maximum NH₄-N, NO_3 -N, total N, and phosphate concentrations (mg L⁻¹) recorded for WS78 were 0.33, 0.23, 1.93, and 0.30,

		2006	2007	2008	2009	2010	2011	2012
рН	WS80	6.7(5.8-8.8)	7.8(6.9-8.4)	8.5(8.1-9.5)	6.0(5.5-6.3)	6.4(5.9-7.2)	6.0(5.3-6.2)	5.9(4.8-6.4)
	WS79	6.4(5.5-7.5)	7.5(6.1-8.3)	8.0(7.4-8.6)	NA	6.2(5.6-7.1)	5.7(5.5-6.2)	5.7(4.9-6.2)
	WS78	6.6(5.8-7.3)	7.6(5.7-8.8)	6.9(5.4-8.7)	NA	6.0(5.0-7.7)	5.9(4.9-6.4)	5.8(4.9-6.6)
Conduct. (microS/ cm)	WS80	0.2(0.1-0.5)	0.3(0.1-0.5)	0.2(0. 1-0.4)	0.1(0.07-0.2)	0.10(0.06-0.2)	0.1(0.06-0.2)	0.12(0.07-0.2)
	WS79	0.2(0.1-0.3)	0.2(0.1-0.3)	0.16(0.1-0.2)	NA	0.08(0.06-0.1)	0.08(0.06-0.1)	0.07(0.06-0.1)
	WS78	0.2(0.1-0.4)	0.2(0.1-0.3)	0.1(0.01-0.3)	NA	0.05(0.01-0.1)	0.08(0.05-0.1)	0.08(0.07-0.1)
DO (mg L ⁻¹)	WS80	3.3(0.4-8.8)	4.4(1.6-11.2)	4.5(2.0-7.8)	3.5(0.8-8.1)	4.6(2.0-8.8)	3.2(1.2-6.3)	4.2(1.4-7.9)
	WS79	2.9(0.3-8.8)	3.9(0.9-12.4)	5.8(1.7-10.0)	NA	4.6(1.4-10.2)	2.5(0.7-7.7)	2.8 (1.0-5.9)
	WS78	5.1(1.4-11)	5.7(1.4-14.3)	6.7(1.6-12.0)	NA	7.5(1.6-12.9)	4.5(0.9-8.8)	4.9(0.9-11.2)
Temp. (ºC)	WS80	20(6.4-29)	18.4(5.8-30.2)	13.4(6.0-21.0)	11.7(7.4-14.3)	13.7(4.4-27.2)	18.6(8.1-27.7)	17.0(4.7-26.1)
	WS79	20(6.6-27)	18(5.6-29.7)	12.9(4.8-20.5)	NA	13.6(4.8-26.7)	16.8(5.5-27.3)	16.6(5.1-25.7)
	WS78	20(6.8-28)	18.6(5.6-29.6)	17.8(4.6-26.2)	NA	12.3(3.7-27.3)	19.5(8.8-27.7)	16.7(4.4-26.8)

Table 1—Annual mean of physical and chemical parameters for WS80, WS79, and WS78 with ranges in parentheses

DO = Dissolved oxygen, Conduct. = Stream conductivity, Temp. = Temperature, NA = Data not available

respectively. The NO₃-N concentrations for all watersheds from 2006 to 2012 did not exceed drinking water standard value, 10 mg L⁻¹, reported by USEPA (2000).

Nitrogen and phosphate concentrations varied with rain received with years receiving highest rainfall registering lower concentrations, and this was attributed to dilution effects. The dilution effects due to increasing flow volumes on nutrients have been reported by Lynch and Corbett (1990). Differences in flush effects after dry periods of the year could also lead to variability within and between annual mean nutrient concentrations. Elevated nutrient concentrations soon after long dry periods were associated with flush effects (Amatya and others 1998, 2009). The systematic decrease in inorganic N and phosphate from 2006 to 2012 for WS80 was attributed to increased uptake since the site was undisturbed. The annual mean phosphate concentrations for WS80 were greater than WS79 concentrations probably due to lower flow for WS80 than WS79. Since WS77 and WS80 drain to form WS79, and WS77 has been reported to register higher flow than WS80 (Amatya and others 2006, 2007) due to greater slope and periodic prescribed burning that reduces vegetation cover on WS77, greater organic N and phosphate concentrations were recorded for WS80. Plants might have preferred inorganic N than organic N and since no inorganic fertilizers were applied to WS80, greater organic N than inorganic N was recorded for the watersheds. Amatya and others (2009) also reported higher NH₄-N concentration than NO₃-N for WS78 when analyzing data for the period, 2006 to 2008. Wilson and others (2006) also reported

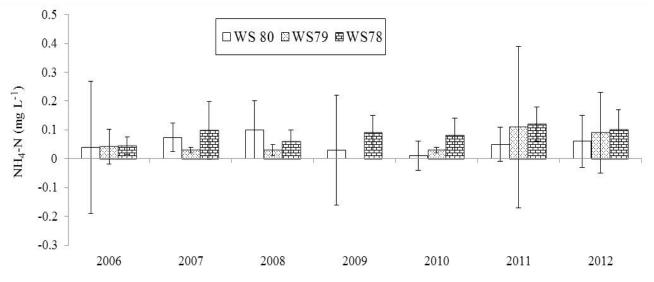


Figure 2—Annual mean ammonium nitrogen concentration as a function of time for a first order (WS80), second order (WS79), and third order watershed (WS78). Bars represent standard deviations of the mean.

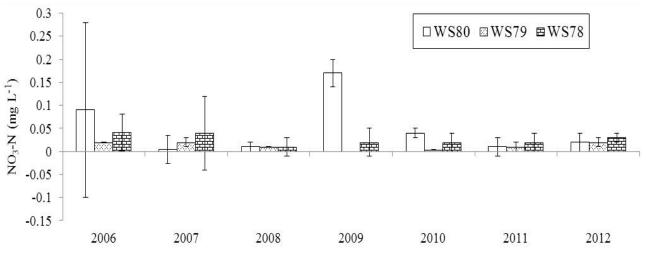


Figure 3—Annual mean nitrate nitrogen concentration as a function of time for a first order (WS80), second order (WS79), and third order watershed (WS78). Bars represent standard deviations of the mean.

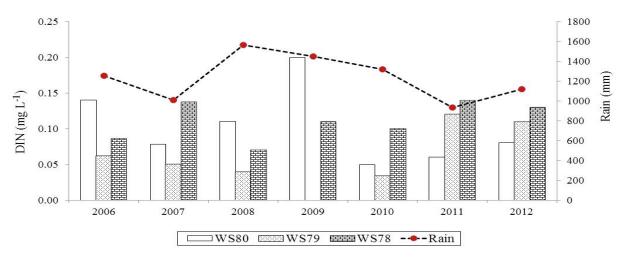


Figure 4—Annual mean dissolved inorganic nitrogen concentration as a function of time for a first order (WS80), second order (WS79), and third order watershed (WS78).

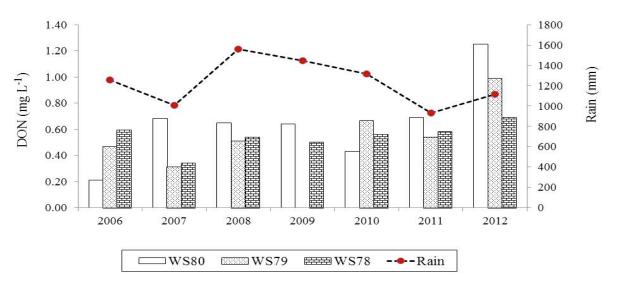
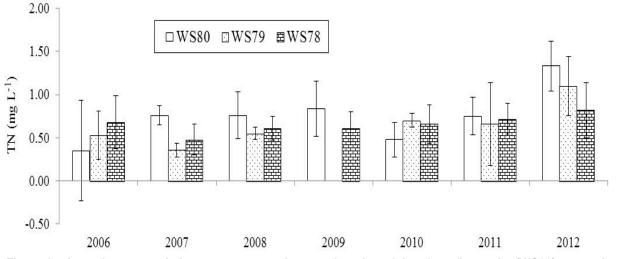
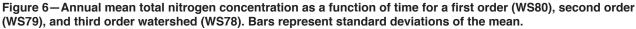


Figure 5—Annual mean dissolved organic nitrogen concentration as a function of time for a first order (WS80), second order (WS79), and third order watershed (WS78)





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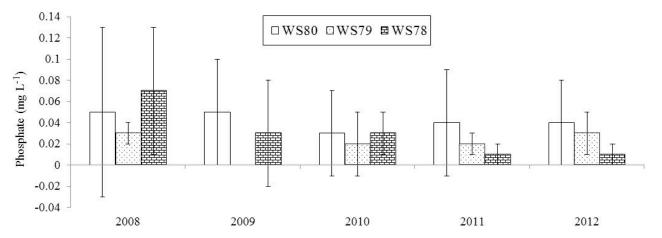


Figure 7—Annual mean phosphate concentration as a function of time for a first order (WS80), second order (WS79), and third order watershed (WS78). Bars represent standard deviations of the mean.

greater organic N than inorganic N with historical data. Other probable reasons for variabilities in nutrient concentrations among watersheds could be differences in watershed drainage areas, land uses, vegetation types, and plant uptake. For example, Lu and others (2005) reported that small scale watersheds have greater heterogeneity than large scale watersheds.

CONCLUSIONS

Variations in N and P concentrations and pH, DO, conductivity, and stream temperature from 2006 to 2012 for all watersheds were likely influenced by rainfall received, differences in plant nutrient uptake, constituents (vegetation type and cover), differences in land uses, and watershed areas. The dominant N component for all watersheds was organic N and the watershed that had the highest DON also registered the highest total N. Phosphate concentration showed a systematic decreasing trend from 2006 to 2012 for WS80 and WS78.

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