1-1-2012

Flux and Source of Dissolved Organic and Inorganic Constituents in Managed Headwaters of the Upper Gulf Coastal Plain, Mississippi

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A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Forestry
in the Department of Forestry

Mississippi State, Mississippi

December 2012

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Title of Study: Flux and source of dissolved organic and inorganic constituents in managed headwaters of the Upper Gulf Coastal Plain, Mississippi

Pages in Study: 45

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Headwater watersheds initiate material export to downstream environments. A nested headwater study examined the flux and source of dissolved constituents and water from a perennial stream and four ephemeral/intermittent streams in the Upper Gulf Coastal Plain, Mississippi. Water was collected during storm and baseflow conditions. Multiple linear regression was used to model constituent concentration and calculate flux. Source of water was determined using principle components analysis and end-member mixing analysis. Rain was the major source of water discharged from the ephemeral and intermittent streams, while groundwater was the major source for water discharged by the perennial stream during events. Baseflow from both stream types was dominated by groundwater sources. The perennial stream had an area weighted average yields of 10.1, 0.01, 1.0, 0.6, and 0.03 kg^{-1} ha^{-1} yr^{-1} of DON, NO_3^--N, NH_4^+-N, PO_4^{-3}, and DOC, respectively. This research highlights the interaction of source water and dissolved constituent flux.

Keywords: headwaters; source; flux; hydrologic event; hydrogeochemistry

ACKNOWLEDGEMENTS

I would like to thank Dr. Jeff Hatten, Janet Dewey, Dr. Byoungkoo Choi, Jason Mack, and Joanna McInnis for all their help and input on this project. I am grateful for my wife Amanda Mangum for putting up with me through this journey and always being there for me. I would also like to thank my graduate committee members Dr. Jeff Hatten, Dr. Robert Kröger, and Dr. Ying Ouyang for their insights and guidance on this project. I would like to acknowledge Weyerhaeuser, U.S. Forest Service, U.S. Geological Survey, National Council for Air and Stream Improvement, and Mississippi Water Resources Research Institute for funding the project. I would also like to thank Mississippi State University and the College of Forest Resource for financial support.

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CHAPTER I

INTRODUCTION

Headwater watersheds are the uppermost areas of drainage basins which initiate stream flow and are important components of the river network with regard to non-point sources of constituents (Nadeau and Rains, 2007). These non-point sources are dominant riverine fluxes to coastal regions throughout the world (Howarth et al., 1995). The nitrogen flux in many temperate regions has increased 2 to 20 times from preindustrial levels as a result of fertilizer use and land use changes. Dissolved nitrogen transported from managed systems (predominantly agriculture, but also forestry, and urban areas) have led to eutrophication and subsequent hypoxia in the Gulf of Mexico (Lopez-Veneroni and Cifuentes, 1994) Furthermore, headwater streams transport a wide range of material such as nutrients, dissolved organic carbon, aquatic and terrestrial invertebrates to downstream reaches. These materials play key roles in the structure, function, biodiversity, and productivity of riverine ecosystems (Wipfli et al., 2007). Understanding the source of dissolved constituents from headwaters streams can help us understand the source of pollutants and nutrients which is important for protecting water quality.

Headwater streams are characterized by distinctive geological features (e.g. geologic composition, stratigraphy, and aquicludes), hydrological (e.g. surface and ground water flow paths), biological (e.g. microbiota and vegetation) and chemical (e.g. availability of electron donors and acceptors) processes (Nadeau and Rains, 2007; Triska et al., 2007; Gomi et al., 2002). Headwater streams can be ephemeral, intermittent, or perennial depending on the channel bottoms elevation above the water table. Ephemeral streams only flow in response to precipitation events with little connection to the water table. Intermittent streams typically flow during the wet season when the water table is elevated. Perennial streams flow year round except for during the most extreme droughts and have a channel below the water table. Storms are of particular importance in discharging water and constituents from headwater streams, and the majority (~90%) of dissolved and particulate material in headwater streams is exported during storm events (Wipfli et al., 2007).

Nitrogen yield from the Southeast United States is in the upper 1/3rd percentile of global nitrogen flux, but is in the lower 1/3rd of phosphorus flux. Headwater streams play an important role in transferring these materials from the land to aquatic systems (Howarth et al., 1995). Headwater streams are not evenly distributed throughout the U.S. The eastern U.S. is highly concentrated with headwater streams due to its humid to sub-humid hydrologic landscape regions. In Mississippi, headwater streams represent 58% to 100% of the total stream length many of which are in in managed forests (Nadeau and Rains, 2007). Research conducted in headwaters of Mississippi found that land disturbance adjacent to streams can be a major factor affecting surface water quality (Carroll et al., 2004). However, current Mississippi Forestry Commission best management practices (BMP's) have no harvest regulations on zero-order streams (Mississippi Forest Commission, 2008). Therefore, it is important to understand the functions of headwater streams to better predict the response of these systems to management disturbances.

Increased understanding of headwater watersheds will allow managers to reduce nutrient and pollutant export by improving BMP's. Research conducted on the Upper Gulf Coastal Plain of Mississippi found that harvest activities adhering to BMPs, such as stream side management zones (SMZs) in headwater watersheds, can reduce water quality impacts from non-point source pollution and maintain hydrologic function (Carroll et al., 2004). However, Carroll et al. (2004) did not examine storm events and fewer studies have examined ephemeral headwater watersheds and how these flashy headwaters connect to downstream reaches.

This study, examined the mechanisms by which water and nutrients are exported from headwater watersheds during important transport events (e.g. storms) and provided insights that will help improve forestry BMPs in the Upper Gulf Coastal Plain. The first of two objectives of this study was to determine the flux of dissolved constituents in ephemeral and perennial streams to better understand how transport processes differ between perennial and ephemeral. The second objective was to determine the source of water in streams throughout storm events and seasons.

CHAPTER II

METHODS

Site and study description

The study site was a small-scale headwater watershed in Webster County Mississippi U.S.A. in the Hilly Gulf Coastal Plain province of the Upper Gulf Coastal Plain (33^{o}30’54.35” N, 89^{o}25’49.39” W; Figure 1). There were three soil series present on the site. The majority of the site was side slopes underlain by the Sweatman soil series (fine, mixed, semiactive, thermic Typic Hapludults). The ridge tops were of the Providence series (fine-silty, mixed, active, thermic Oxyaquic Fragiudalfs) while the floodplains were of the Oaklimeter soil series (coarse-silty, mixed, active, thermic Fluvaquentic Dystrudepts). The Sweatman soil series is well drained with clayey subsoil over stratified shaly and sandy parent materials. Typical soil horizons of the Sweatman are 0 to 15 cm of A horizon silt loam followed by Bt horizons down to 94 cm of silty clay followed by a C horizon consisting of clay. The Oaklimeter soil series is a deep moderately to well-drained soil series on level areas with silty alluvial parent materials. The Providence soil series is a moderately well drained soil similar to Sweatman, but has a fragipan and is found on ridge tops and upper side slopes.

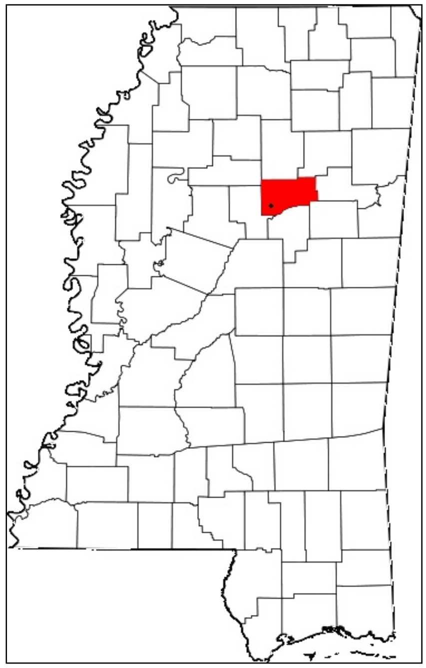


Figure 1 Webster County, Mississippi shown as the red shaded county with the dot indicating the Union Church headwater study area

The average precipitation for the past 30 years was 1,451 mm with average winter (December, January, and February) temperature of 7 °C and summer (June, July, and August) temperature of 26 °C. Precipitation was distributed fairly evenly throughout the year with 53% falling between January and May. Vegetation on the site was characteristic of overstory vegetation in the Southeastern Mixed Forest Province of the Southeastern U.S. (Bailey, 1976). The overstory consisted primarily of loblolly pine (*Pinus taeda* Linnaeus.), various oak species (*Quercus* spp.), yellow poplar (*Liriodendron tulipifera* Linnaeus), sweetgum (*Liquidambar styraciflua* Linnaeus.), various hickory species (*Carya* spp.), American beech (*Fagus grandifolia* Ehrhart) and black cherry (*Prunus serotina* Ehrhart.). The midstory was composed of specimens from the list above as well as eastern hophornbeam (*Ostrya virginiana* (Mill.) K. Koch) and American witchhazel *(Hamamelis virginiana* Linnaeus.). The understory was composed of American beautyberry (*Callicarpa Americana* Linnaeus.), red buckeye (*Aesculus pavia* Linnaeus.) and switchcane (*Arundinaria gigantea* Michaux.). In areas where harvest actions have opened the canopy, blackberry species (*Rubus* spp.) were the dominant cover.

The ephemeral and intermittent sub-watersheds are nested within the perennial watershed which drains the entire study area. There are a number of intermittent and ephemeral streams within the perennial watershed, of these streams. Four were chosen for examination. The four monitored sub-watersheds have intermittent to ephemeral streams with treatments that are representative of forest management in the Southeast. The treatments were part of a larger study of the effects of forestry on hydrological function of headwater streams, but were not a focus of this study. However, these treatments do represent a range of watershed conditions encountered on similar sites in the Upper Gulf Coastal Plain. The watersheds were harvested in October of 2007 and had four different stream side management zone (SMZ) treatments. The reference (UC1) was not harvested, UC2 was clear-cut and had a SMZ with logging debris in the drainage channel, UC3 was clear-cut and had a SMZ without logging debris in the drainage channel, and UC4 did not have a SMZ and was clear-cut with all merchantable timber removed. The perennial stream watershed (UCP) encompassed the ephemeral and intermittent streams' watersheds which included 20.6 ha of unmonitored floodplain and ephemeral and intermittent drainages (Table 1).

Table 1 Stream class, area, total discharge, and maximum discharge in ephemeral, intermittent, and perennial streams of the Union Church research site in Webster County, Mississippi

Watershed	Stream Class*	Area (ha)	Total Discharge ($x\ 10^3\ m^3\ yr^{-1}$)	Maximum Discharge ($l\ s^{-1}$)
UC1	Intermittent	2.39	27.13	0.64
UC2	Intermittent	3.63	5.49	0.13
UC3	Intermittent	3.83	27.79	1.18
UC4	Ephemeral	1.80	4.99	1.00
Ungaged	Ephemeral	20.56	173.51	N/A
UCP	Perennial	32.21	239.91	47.32

*Stream class based on the percent of year with water present as measured during this study

Sampling methods

At the outlet of each watershed there was a 1.8 m long, 254 mm diameter section of schedule 40 polyvinyl chloride (PVC) pipe. Event samples were collected during storm events. Baseflow samples were collected when discharge was at a steady state with very little to no change in the hydrograph. Grab water samples were collected during monthly field visits to represent baseflow at all site locations when conditions allowed. Discharge of the ephemeral and intermittent streams was calculated using a 750 ISCO area velocity sensor that recorded water depth and velocity and calculated water discharge from the pipe. An ISCO 2900 discrete water sampler was used to collect event water samples. The sample collection tube was attached to the downstream end of the pipe. All data were recorded in an ISCO 4150 flowlogger programmed using Flowlink to sample during events that overcame a discharge or stage threshold. Discharge on the perennial stream was calculated using a stage-discharge rating curve. Stage was measured using a pressure transducer (In-Situ LevelTroll 300) inside a stilling well (1.8 m tall, 152 mm diameter, schedule 40 PVC pipe) mounted to a T-post in the center of the perennial stream. The stream profile was measured and rating curve developed from 15 discharge measurements made with a Marsh-McBirney Flo-Mate. The perennial stream was instrumented with an in-situ 750 ISCO area velocity sensor attached to a T-shaped metal pipe buried in the center of the stream with the sensor near the bottom of the stream. Velocity and stage data from the area velocity sensor was used to trigger sample collection. Stream monitoring equipment was installed on all watersheds on 2/17/2010 and removed on 7/13/2011.

There were 25 wells per SMZ treatment at five m intervals with a total of 100 ground water wells, the depth of each pipe was 1-3 m depending on location (Figure 2). Well water samples were collected using a plug well sampler during monthly field visits as conditions allowed. Ground water wells were split into valley, floodplain, and hillslope categories because spatial and elevation differences may alter the water chemistry. Valley groundwater wells were 20 m apart and located in the channel of the ephemeral and intermittent watersheds 20-100 m upslope of the sub-watershed outlet (four wells per watershed). Floodplain groundwater wells were 5 m apart and located at the lowest most point of the sub-watersheds in the floodplain of the perennial stream and were characterized by flat topography (five floodplain wells per sub-watershed). Hillslope groundwater wells were located on either side of the valley wells with eight wells distributed evenly on the side slopes and ridge positions (16 wells per sub-watershed).

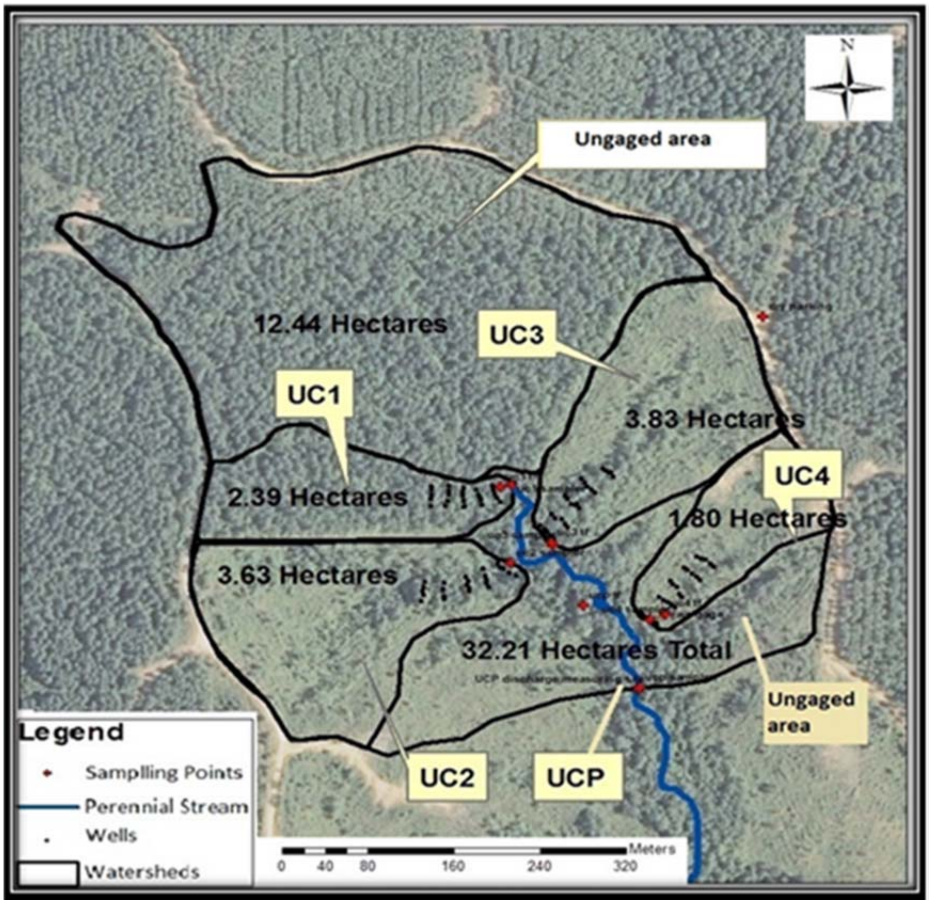


Figure 2 Map of the Union Church headwater study area in Webster County, Mississippi where samples were collected between February 2010 and May 2011

An ISCO 674 tipping bucket rain gage was located in an open area of UC4 (clearcut) to collect precipitation data, it was installed on 5/30/2010 and removed on 7/13/2011. Precipitation data collected at 15 minute intervals from a NOAA weather station located in Eupora, Mississippi (33.54°N, 89.27°W) was utilized for the period of time when data from our tipping bucket rain gage was unavailable (2/17/2010 to 5/30/2010). Rainfall for chemical analysis was collected using an acid washed plastic 18.9 L bucket with an acid washed nylon window screen over the top to prevent contamination by litter. The bucket was placed in an open area in UC4 (clearcut). Throughfall was collected using three similar devices placed in the understory of UCP, UC3, and UC1. Soil water was sampled using zero-tension passive lysimeters at three soil depths (O, A-10 cm, and A-20 cm). Throughfall, rain, and soil solutions were collected during field visits within a week of a storm event.

Laboratory Methods

Samples were filtered through a glass fiber filter (GFF) 0.7 µm filter (Whatman 47) and analyzed for DOC, DON, DIN, ultraviolet absorbance (UVA), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{-3}), sulfate (SO_4^{-2}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{+2}), and calcium (Ca^{+2}). Constituents NO_3^- and NH_4^+ were converted to NO_3^- -N and NH_4^+-N. Filtered water samples were sent to the UC Davis Stable Isotope facility for determination of DOC using an OI Analytical Model 1030 TOC Analyzer (OI Analytical, College Station, TX). The samples were acidified and purged with helium to remove all dissolved inorganic carbon. Filtered samples were also analyzed for UVA at 254 nm by an ultraviolet (UV) spectrophotometer Biomate 3 scanning spectrophotometer-single beam (Thermo scientific Sunnyvale, CA). Anions were determined using standard ion chromatography methods APHA 4110 (APHA et al., 2005) and cations values were determined using the ASTM D6919-09 (ATSM, 2011) method for dissolved alkali and alkaline earth cations. Anions and cations were determined using a Dionex ion chromatograph DX 500 chromatograph system with a GP 40 gradient pump a ED 40 electrochemical detector enclosed in a CC 20 chromatography enclosure (Dionex, Sunnyvale, CA). Dissolved inorganic nitrogen was calculated as the sum of NH_4^+-N and NO_3^--N. A 9 ml sub-sample was microwave digested in 2ml of digesting solution containing 3.83 M sulfuric acid and 9.23 mM mercuric oxide. The samples were digested using a MARS X Press microwave digestion system (CEM, Matthews, NC) for a total of one hour with a 15 minute ramp time and 45 minute hold time at 200°C. This procedure converts all dissolved nitrogen to NH_4^+-N and a Technicon Autoanalyzer III wet chemistry analyzer (Bran+Luebbe, Norderstedt,Germany) was used to determine Total NH_4^+-N (Lo et al., 2005). DON was calculated by the difference of total nitrogen and DIN. All calibration curves were linear with a R^2 of 0.995 to 0.999.

Data analysis

Flux calculations

Flux from the gaged watersheds was calculated over the entire length of the study period by modeling the concentration of each constituent and multiplying it by measured water discharge. Constituent concentrations were modeled to determine concentrations for those periods when samples were not collected. The ungaged area was assumed to behave similarly to the gaged area. Therefore an area weighted summation of water and constituent fluxes from the gaged ephemeral/intermittent watersheds was used to determine the contribution of water and constituents to the perennial stream by the ungaged ephemeral/intermittent streams within the watersheds.

Multiple linear regression with indicator variables was used to define the models of constituent concentration for those periods in which no constituent concentration was available. Prior to model development the histogram of each variable was examined for normality and log-transformed if necessary. Normality was determined prior to developing the model by comparing a histogram of the data to a fitted normal or log-normal curve. Precipitation, water year day, discharge, time since event, and the rate of change in discharge were utilized as independent variables. Time since event in the ephemeral/intermittent streams was defined as any discharge >0.002 m^3 sec^{-1} or the rate of change in discharge was >0.0002 m^3 sec^{-1} 15 $minute^{-1}$ or flow was initiated. A new event was also considered if there was one hour of decline in discharge. Time since event in the perennial streams was defined as any discharge >0.002 m^3. Since each watershed may have unique constituent discharge characteristics indicator or indicator variables were utilized as additional independent variables to distinguish between the watersheds. Initially, all independent variables were input into the model and stepwise removals were continued (using independent variable criteria of $p \leq 0.05$ for inclusion, $p \geq 0.1$ for removal) until all non-significant variables had been removed and a statistically significant model was achieved ($p < 0.001$). Prior to stepwise removal of non-significant variables, the initial linear model of constituent concentration (C) took the form of:

$$C = \beta_1 * UC1 + \beta_2 * UC2 + \beta_3 * UC3 + \beta_4 * UC4 + \beta_5 * UCP + \beta_6 * P + \beta_7 * WY + \beta_8 * Q + \beta_9 * TE + \beta_{10} * RT + \beta_0 \quad (1)$$

(1) Where β_0 - β_{10} are the linear regression coefficients associated with each variable, UC1-UCP were indicator variables that equal one when modeling concentration for that particular watershed and zero otherwise, P was the previous 15 minutes of precipitation, WY was the water year day (days since October 1), (Q) discharge was instantaneous discharge, TE was the time since the beginning of an event, and RT was the rate of change of the instantaneous discharge.

The flux of chemical constituents DON, NO_3^--N, NH_4^+-N, PO_4^{-3}, and DOC was calculated every 15 minutes over the entire study period (i.e. 15 months = 1.25 years). Total flux was determined by summing the flux for each 15 minute interval (kg yr^{-1}) and yield (kg ha^{-1} yr^{-1}) was calculated by dividing the flux by the area of the watershed.

Source and end member mixing analysis

The source of water was determined by comparing the chemical characteristics of stream samples to that of throughfall, precipitation, O and A horizon soil solutions, and groundwater using end member mixing analysis (EMMA; Burns et al., 2001). End-members consisted of 67 well samples, 48 throughfall samples, and 11 soil solution samples. After end-members were established, a specific stream water samples similarity to each end-member explained the contribution of each end-member to that sample.

Solutes that do not react during transport are considered conservative and used in EMMA. Only dilution and/or mixing are allowed to change the concentration of constituents in solution. Constituents that behave the same over multiple events and are stable in the end-members were chosen as conservative tracers to envelop the stream water data (Yevenes and Mannaerts, 2012).

Principal component analysis (PCA) was used to reduce the number of those parameters (constituents) found to behave conservatively and produce principle components. The constituents chosen for PCA were normalized by dividing the concentration of each samples constituent by its standard deviation giving each parameter equal weight (Tesi et al., 2010). Principal component analyses was performed on individual watersheds using R 2.14.2 on all stream samples as well as end-members (throughfall, well, and soil solution) for each chemical chosen. The analysis resulted in six principle components. Finally, EMMA was implemented to solve for the proportion of each end member that contributes to the stream water (Christophersen and Hooper, 1992). Extreme samples were chosen as end-members to encompass the largest amount of data (Brown et al., 1999). UC1-UC4 used the same extreme end-members. The end-members were valley well groundwater, rain, and O-horizon. UCP used the same extreme end-members with the exception of floodplain in place of valley well groundwater.

The proportion of each stream sample that was comprised of each end-member was determined using an end-member mixing model (Tesi et al., 2010). The model used the distance between end-members and samples as the relative influence of an end-member on a sample. Scores from principle component one and principle component two for all streams and extreme end-member samples were used as variables in determining source.

Statistical analysis

Flux, source of water, precipitation, water year, discharge, lag time, and time of concentration (TOC) were the relationships at individual watersheds that were examined using Pearson correlations (α=0.05). Time of concentration was calculated as the time from beginning of precipitation to the peak in discharge for each event. Lag time is the time from the beginning of precipitation to the initiation of discharge in ephemeral streams. Lag time and TOC will be used to examine the effect of storm intensity on nutrient flux. In intermittent and perennial streams lag time is the time from the beginning of precipitation to discharge above baseflow.

To determine how each watershed varied ANOVA was implemented to find similarities and differences between watersheds and the actual constituent concentrations. Analysis of variance (ANOVA) was used to compare concentrations among the watersheds with all watersheds and by constituent at an (α=0.05).

Some studies in the region may have not thoroughly characterized constituent concentrations in water discharged from watersheds due to sampling procedures that did not adequately take into account the effect of storms on nutrient and pollutant flux (e.g. Carroll et al., 2004). The biggest drawback of those studies was the collection of samples based on intervals of time, as opposed to intervals of discharge. This study collected discrete samples over events while grab samples were taken during field visits at baseflow. The odds of collecting event samples while sampling at regular time intervals is small since storm flow typically make up a very small portion of the time. In this study we are able to compare our results to others by calculating average concentrations that were not biased by flux (e.g. discharge) and averages that are biased (e.g. raw averages). The unbiased average concentration is the discharge weighted average (e.g. NO_3^{-1}-N yield divided by water yield). The biased average concentration was calculated using the modeled NO_3^--N concentration of all points thereby weighting each concentration modeled at 15 minute intervals evenly. These calculations allowed for a direct comparison with other studies and a better understanding of the importance of storm events.

CHAPTER III

RESULTS

Hydrometric observations

There were marked differences between event and baseflow in both stream types. Events made up 72% of the total discharge in the ephemeral and intermittent streams. In the perennial stream events only make up 25% of the total discharge with baseflow making up the remaining 75%. This highlights the significance of events in headwater areas.

There were many precipitation events but only16 events generated discharge in one or more of the ephemeral and intermittent streams. Over the 15 month study period 94% of the discharge events occurred between January and May while precipitation falling between January and May accounted for 53% of the total annual precipitation. The duration of events varied from one hour to 22 hours and 15 minutes with the average event lasting eight hours. Time of maximum precipitation was typically observed near the beginning of events.

Total precipitation per event was highly variable with an average of 55 mm and varied greatly over the year (Table 2). Between January and May the area became saturated and baseflow occurred due to a high water table and low evapotranspiration early in the growing season. UC1 and UC3 had baseflow from March to April, while

UC2 had baseflow between January and March. UC4 had no baseflow over the study period while the perennial stream had water flowing throughout the year.

Table 2 Precipitation event descriptions at the Union Church headwater research area in Webster County, Mississippi, data collected between February 2010 and May 2011

Event	Date	Event Duration (hour)	Max Precipitation Rate (mm/hour)	Total Precipitation (mm)	Water Year Date
1	2/4/2010	16.45	10	81	126
2	3/11/2010	1:45	20	28	161
3	3/21/2010	5:45	13	21	171
4	4/3/2010	1:00	61	18	184
5	4/23/2010	6:30	72	110	204
6	4/30/2010	2:45	63	61	211
7	5/2/2010	10:45	58	66	213
8	11/29-30/2010	22:15	51	61	59-60
9	12/31/2010-1/1/2011	4.15	56	82	91-92
10	1/25/2011	17:30	10	38	116
11	3/8-9/2011	18.30	19	58	158-159
12	3/14-16/2011	4:00	20	24	164-166
13	4/4/2011	4.45	30	46	185
14	4/15/2011	4.15	58	89	196
15	4/20-21/2011	5.00	15	51	201-202
16	4/27/2011	3:30	22	41	208

The average event discharge calculated as all discharge measurements averaged over the event from the ephemeral and intermittent streams was 0.41 L s^{-1} while the average discharge from the perennial stream was 11 L s^{-1} over all storms. There was high variability between events and watersheds with respect to discharge and total discharge over events. The average total discharge over an event at the ephemeral and intermittent streams was 749 cubic meters (m^3), at the perennial stream the average was 4,324 m^3 (Table 3). Assuming that the ungaged area discharges water at the same rate as the gaged ephemeral and intermittent areas then this area discharged 72 m^3 ha^{-1} during events, compared to the perennial stream which discharged 134 m^3 ha^{-1}. If the largely unharvested ungaged area is assumed to behave similarly to the reference then the total intermittent and ephemeral area discharged 111 m^3 ha^{-1} which is much closer to that of the perennial. This suggests that the ungaged area is behaving like the uncut reference.

Table 3 Event discharge and total discharge during events between February 2010 and May 2011 at the Union Church headwater research area in Webster County, Mississippi

		UC1	UC2	UC3	UC4	UCP
Discharge over events (L s^{-1})	Average	0.39	0.07	0.73	0.45	11
	Minimum	0.02	0.02	0.01	0.03	0.1
	Maximum	0.64	0.10	1.18	1.00	47
Total discharge over events (m^3)	Average	597	199	1816	384	4324
	Minimum	57	24	30	12	306
	Maximum	1704	485	9393	977	14900

There were a number of general watershed relationships noted. Water year and duration of event had a negative relationship implying that as the water year progressed the duration of event decreased (R=-0.62 and p=0.01). Shorter storms tended to be higher intensity which led to a significant positive relationship between TOC and duration (R=0.58 and p=0.01), lag time and duration (R=0.57 and p=0.02), and lag time and TOC (R=0.64 and p=0.02) for all watersheds. These results suggest that the routing of water through a watershed is different between high intensity storms and low intensity storms. It follows then, that the movement of dissolved constituents will also be affected by storm intensity and timing.

The average time of concentration (TOC) varied from five hours and 22 minutes to ten hours and 20 minutes (Table 4). Sub-watershed UC2 (intermittent) had the shortest average TOC and UCP (perennial) had the longest TOC as expected due to watershed size. The minimum TOC was found to be zero hours during a very high intensity rain with a maximum time of 34 hours during a slow steady rain. The average lag time varied from two hours 39 minutes to nine hours and 50 minutes with UC2 having the shortest lag time while UC4 had the longest.

Table 4 Time chart depicts event timing by watershed between February 2010 and May 2011 at the Union Church headwater research area in Webster County, Mississippi

		UC1	UC2	UC3	UC4	UCP
Time of concentration (TOC) (hour)	Average	6:35	5:22	7:23	8:48	10:20
	Minimum	0:00	0:30	0:00	0:30	0:15
	Maximum	21:30	21:30	22:45	25:00	34:00
Events time from precipitation to beginning of flow (Lag Time) (hour)	Average	3:55	2:39	5:34	9:50	8:45
	Minimum	0:00	0:00	0:00	0:00	0:00
	Maximum	8:30	3:45	19:00	21:00	22:00

Characteristics of dissolved constituents

Over the study period there were 16 storm events but only 12 events were sampled. The events varied in size from large storms which caused almost all stream samplers to collect samples to very small events where fewer samples were collected. Over these events 232 samples were collected along with 80 baseflow samples over the study period (Table 5).

Table 5 Total number of samples collected over study period and maximum number of samples collected over a given storm at the Union Church headwater research area in Webster County, Mississippi between February 2010 and May 2011

Sample Location	UC1	UC2	UC3	UC4	UCP
Total number of samples	63	80	13	39	31
Maximum samples per event	25	23	6	14	15

Stream sample and end-member constituent concentrations were highly variable between sample locations (Table 6). Baseflow samples had the highest average concentrations of Cl^-, SO_4^{-2}, NH_4^+-N, and Na^+. We expect that the primary source of baseflow is groundwater suggesting that these constituents were concentrated in the subsurface source. The results suggest that our expectation was correct with groundwater being the primary source of baseflow. Event flow samples had the highest concentrations of DOC, NO_3^--N, PO_4^{-3}, K^+, Mg^{+2}, Ca^{+2} and DON, suggesting that these constituents are concentrated in those sources from more rapid shallow lateral flow. The O-horizon samples had the highest average UVA and concentrations of DOC, K^+, Mg^{+2}, Ca^{+2} and NH_4^+-N, which suggests that stream water that is derived from shallow lateral flow will be enriched in these constituents. Event flow samples were also enriched in these constituents, suggesting that rapid lateral flow is contributing strongly to event samples. By comparing constituent concentrations from different sampling locations the first evaluation of source of water can be made.

Table 6 Average constituent values by all sample types of samples collected at the Union Church headwater research site in Webster County, Mississippi between February 2010 and May 2011

Sample type	Stream samples				Groundwater						Precipitation				Soil solutions					
	Event		Baseflow		Upslope		Valley		Floodplain		Rain		Throughfall		O-Horizon		A-10cm		A-20cm	
	x□	σ	x□	σ	x□	σ	x□	σ	x□	σ	x□	σ	x□	σ	x□	σ	x□	σ	x□	σ
	Absorbance																			
UVA	0.53	0.25	0.05	0.11	0.15	0.16	0.12	0.10	0.16	0.23	0.02	0.02	0.40	0.36	1.48	0.26	0.71	0.26	0.75	0.08
	$mg\ L^{-1}$																			
DOC	13.9	5.12	0.96	0.33	3.65	1.64	3.17	2.28	1.21	0.41	1.89	1.75	20.2	26.6	27.7	7.63	17.3	10.2	12.2	5.97
Cl^-	1.73	0.88	3.19	0.91	2.49	0.64	4.21	1.66	4.33	1.88	0.80	0.23	2.01	1.68	1.63	0.53	2.40	0.83	2.38	1.10
NO_3^--N	0.18	0.31	0.01	0.02	0.17	0.36	0.06	0.24	0.03	0.06	0.14	0.08	0.25	0.30	0.06	0.05	0.02	0.02	0.00	0.00
PO_4^{-3}	0.11	0.17	0.04	0.02	0.66	0.00	0.06	0.00	0.03	0.00	0.08	0.08	0.27	0.39	0.46	0.30	0.08	0.00	*	*
SO_4^{-2}	3.27	1.60	5.50	2.98	3.36	1.13	3.47	2.21	4.18	2.17	1.21	0.54	1.64	1.01	2.80	0.99	3.02	1.15	1.84	0.41
Na^+	2.00	0.99	4.28	1.35	2.84	0.86	4.25	1.28	4.11	1.29	0.80	0.19	1.37	0.78	1.75	1.42	2.71	1.98	3.03	1.40
K^+	1.78	0.70	1.18	0.57	0.75	0.30	1.48	0.71	0.82	0.33	0.28	0.15	3.66	3.86	9.72	4.86	5.41	1.10	0.36	0.05
Mg^{+2}	1.79	0.89	1.46	0.27	0.67	0.32	0.55	0.39	0.68	0.31	0.24	0.31	0.82	0.74	3.75	1.05	1.49	0.86	1.81	1.02
Ca^{+2}	2.67	0.83	2.00	0.71	0.97	0.62	0.90	0.65	0.76	0.39	0.70	0.38	1.69	1.37	8.60	0.40	5.43	1.21	2.26	0.08
NH_4^+-N	0.05	0.12	0.06	0.10	0.04	0.05	0.16	0.18	0.06	0.09	0.21	0.18	0.15	0.13	0.58	0.64	0.00	0.00	*	*
DON	0.75	0.65	0.70	0.53	0.43	0.20	0.59	0.16	0.60	0.34	0.38	0.17	0.65	0.76	4.16	0.91	0.50	0.12	0.50	0.32

x□ Mean
σ Standard deviation
* Observed value was below detectable limit

Flux of dissolved constituents

Multiple linear regression was used to define the models of constituent concentration (Table 7). NO_3^--N and discharge were log-normally distributed and therefore the regressions were performed log transforming the data of those parameters. A significant model was found between UVA and DOC (R^2=0.900, p<0.001) where DOC (mg L^{-1}) = 25.249*UVA + 1.259. This model was used to model DOC concentrations for those samples that UVA was collected, but DOC was not.

Table 7 Multiple linear regression with indicator variables for constituent concentration calculations at the Union Church headwater research site in Webster County, Mississippi

Constituent	Multiple Linear Regression with Indicator Variables	R^2	p
$\ln NO_3^-$-N	-3.341*UC2 + 1.077*UC3 + 4.434*UC4 – 2.076*UCP + 0.058*TE + 0.099*P + 0.288*lnQ – 3.916	0.765	<0.001
NH4+ -N	0.033*P – 0.002*WY + 0.388	0.377	<0.001
DON	0.548*UC1 + 2.639*UC3 + 0.039*P – 0.009*WY + 1.929	0.540	<0.001
DOC	-0.005*UC1 + 0.0047*UC4 – 0.0192*UCP – 0.00049*TE + 0.00036*P + 0.00327*lnQ + 0.03904	0.539	<0.001
PO_4^{-3}	0.028*P + 0.087	0.223	<0.001

Where: UC1-UCP are indicator variables that equal 1 when modeling concentration for that watershed and 0 otherwise; P is the previous 15 minutes of precipitation; WY is the water year day; lnQ is the natural log of instantaneous discharge; TE is the time since the beginning of an event; and RT is the rate of change of the instantaneous discharge (non-significant predictor for every model)

The average yield of NO_3^--N, NH_4^+-N, DON, DOC, and PO_4^{-3} from the ephemeral and intermittent streams was 0.01, 1.03, 10.09, 0.027, and 0.65 kg ha^{-1} yr^{-1}, respectively. From the ephemeral and intermittent streams to the outlet UCP NO_3^--N, DON, NH_4^+-N, PO_4^{-3}, and DOC flux average decreased slightly while NH_4^+-N increased slightly

(Table 8). While there was much variability between the ephemeral streams the majority of all water and dissolved constituents were exported from the perennial stream, suggesting that there was little processing in the short distance between the ephemeral and perennial streams.

Table 8 Water yield and constituent yield from the Union Church headwater research area in Webster County, Mississippi on data collected from February 2010 to May 2011

Site	Water yield $x10^3$ m^3 ha^{-1} yr^{-1}	NO_3^--N kg ha^{-1} yr^{-1}	NH_4^+-N kg ha^{-1} yr^{-1}	DON kg ha^{-1} yr^{-1}	DOC kg ha^{-1} yr^{-1}	PO_4^{-3} kg ha^{-1} yr^{-1}
UC1	11.351	0.103	0.472	8.400	0.156	1.245
UC2	1.512	0.0004	0.121	0.928	0.027	0.259
UC3	7.255	0.410	1.685	52.980	0.164	1.325
UC4	2.772	2.221	0.350	5.145	0.055	0.513
UCP	7.450	0.008	1.032	10.090	0.027	0.648

Each watershed behaved differently with regard to constituents and their driving factors. As expected, all constituents at all streams had relationships with either total and/or max discharge. However, NO_3^--N, NH_4^+-N and DOC yield of UC4 had a significant negative relationship with lag time (R= -0.557, -0.573, and -0.540 with p=0.031, 0.026, and 0.038, respectively). Since lag time and storm intensity were related this suggests that lower intensity storms exported less NO_3^- -N, NH_4^+ -N and DOC from UC4. Also duration of event and lag time had a positive relationship at UC3, UC4, and UCP with values of (R=0.576, 0.523, and 0.600 with p=0.031, 0.045, and 0.014, respectively). The water year and duration of event had a negative relationship (R=-0.620 and p=0.010) indicating that as the water year progressed the shorter events became. While other constituents and streams did not have significant relationships with storm or hydrograph characteristics indicating other factors are influencing constituent concentration.

The flux weighted average NO_3^--N concentration (i.e. not biased by discharge) from the ephemeral and intermittent streams were 0.0002 to 0.8 mg l^{-1} while the perennial streams value was 0.001 mg l^{-1}. The biased estimate, using non-weighted flux average, of the ephemeral and intermittent streams was between 0.0001 and 0.3 mg l^{-1} and the perennial stream had a value of 0.0005 mg l^{-1}. By collecting samples at regular time intervals the average NO_3^{-1}-N concentration of intermittent and ephemeral streams may be underestimated between 1.4 and 3.8 times and the perennial streams may be underestimated by 2.1 times (Table 9).

Table 9 Flux and non-flux weighted averages of NO_3^--N and difference between flux and non-flux weighted averages for data collected from the Union Church headwater research area in Webster County, Mississippi

Site	Flux weighted average mg l^{-1}	Non-flux weighted average mg l^{-1}	Relative Difference
UC1	0.0091	0.0065	1.39
UC2	0.0002	0.0001	1.77
UC3	0.0565	0.0149	3.79
UC4	0.8011	0.3084	2.60
UCP	0.0010	0.0005	2.05

After ANOVA, NO_3^--N concentrations from UC4 were higher (F=80.42 and p=<0.0001) than all other watersheds (Table 10). DON showed an opposite trend with UC3 and UC1 being significantly higher than UCP, UC2 and UC4. NH_4^+-N and PO_4^{-3} were not significantly different among the watersheds. DOC concentrations were not significantly different among the watersheds except at UCP.

Table 10 DON, NO_3^--N, NH_4^+-N, PO_4^{-3}, and DOC with ANOVA grouping, mean, and number of observations by watersheds at the 0.05 alpha level for event samples collected at the Union Church headwater research area in Webster County, Mississippi between February 2010 and May 2011

Constituent	Grouping	Mean (mg L^{-1})	N	Watershed
NO_3^--N	A	0.66	38	UC4
P-value <0.0001	B	0.15	80	UC2
F-value 80.42	C	0.05	32	UCP
	C	0.02	58	UC1
	C	0.01	14	UC3
DON	A	1.32	13	UC3
P-value <0.0001	A	1.08	64	UC1
F-value 18.05	B	0.77	27	UCP
	BC	0.55	78	UC2
	C	0.42	38	UC4
NH_4^+-N	A	0.09	56	UC2
P-value 0.3924	A	0.07	31	UCP
F-value 1.03	A	0.07	14	UC3
	A	0.04	19	UC4
	A	0.04	33	UC1
PO_4^{-3}	A	0.14	6	UC2
P-value 0.8563	A	0.07	5	UC1
F-value 0.33	A	0.04	3	UC4
	A	0.04	2	UC3
	A	0.04	3	UCP
DOC	A	18.56	7	UC4
P-value 0.0093	A	15.57	9	UC1
F-value 3.74	A	14.80	9	UC3
	A	14.76	28	UC2
	B	9.11	6	UCP

EMMA

Six constituents, SO_4^{-2}, Cl^-, Mg^{+2}, Na^+, NO_3^-, and UVA, were found to mix conservatively and were used in the PCA to simplify the data into two principle components. Principle component one and two were used to plot stream samples and end-members. The source of stream samples whose data were within the bounds of the end-members can be determined. The sources of samples that fell outside this frame were not able to be determined, because the end-members could attribute over 100% of the source.

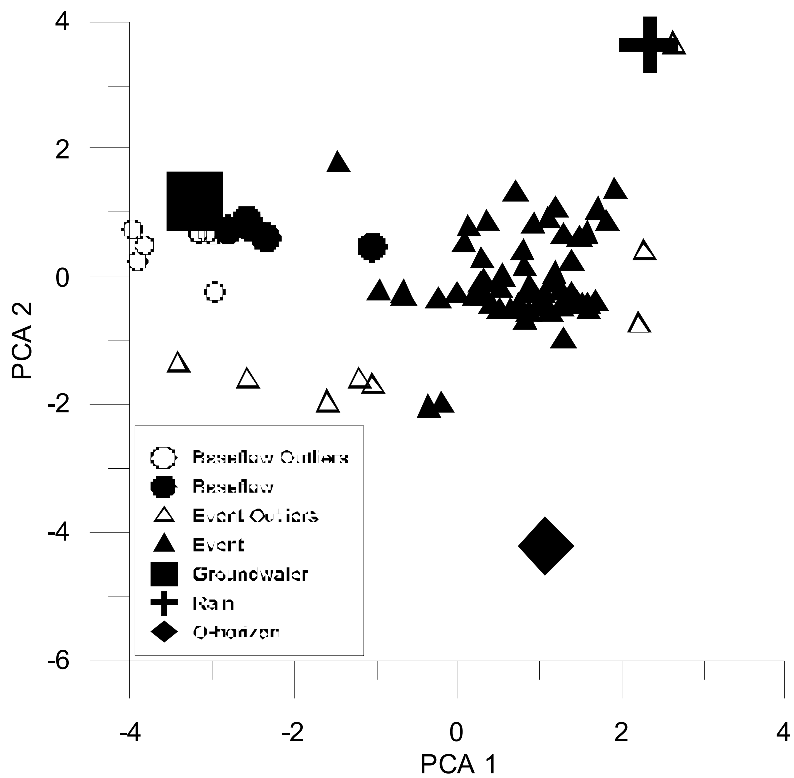
The source of all stream samples could not be determined as a result of insufficient characterization of the end-members or more complex mixing of components that were not captured by the end-members. The first two principle components explained 48% (UCP) to 53% (UC3) of the data (Table 11)

Table 11 Cumulative proportion of the variability explained by principle components one and two by watersheds at the Union Church headwater research are in Webster County, Mississippi on data collected between February 2010 and May 2011

	UC1	UC2	UC3	UC4	UCP
PC1	33%	36%	28%	30%	28%
PC2	53%	53%	50%	53%	48%

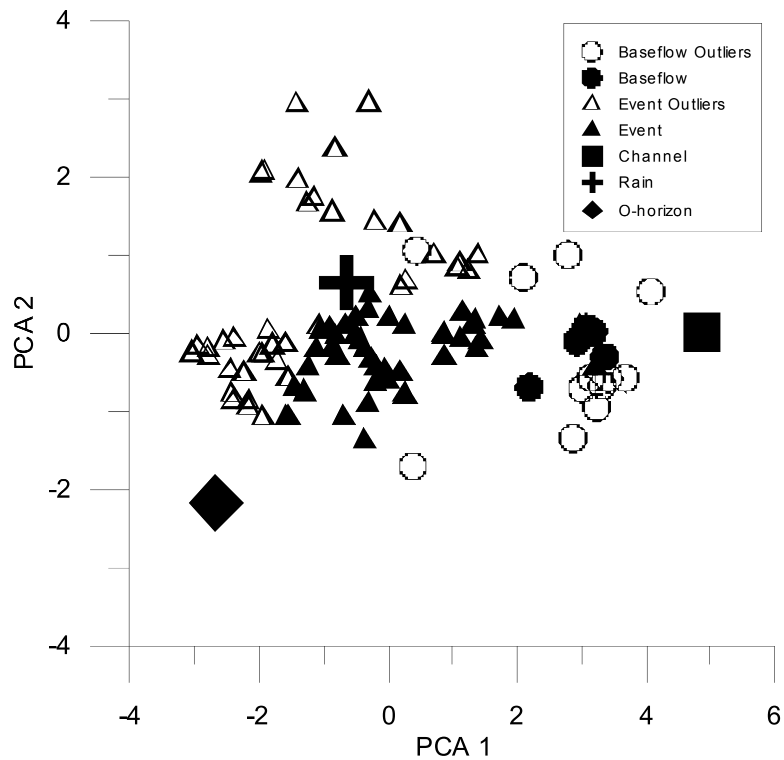
End-member mixing analysis was performed to determine the proportion that each end-member contributes to a given stream sample. End-member samples were chosen as those that best bound the stream sample data, which were those samples that were at the extreme edges of the plotted data. Baseflow from the intermittent and perennial streams was most strongly associated with the groundwater end-member with the exception of UC2. The source of baseflow at UC2 was heavily influenced by the groundwater, but many of the samples fell outside of the area enveloped by the end-members.

The source of water during events varied by watershed and between events. The source of water from UC1 was evenly distributed between rain, O-horizon, and groundwater end-members. Water source from UC2 was different from the other ephemeral and intermittent streams since most of its event samples were heavily influenced by the rain end-member. UC3 had no outliers and event samples fell evenly between all end-members but were more influenced by rain and groundwater. Most event samples from UC4 fell between O-horizon and rain with only one sample near the groundwater end-member. Most of the event stream samples from the perennial stream fell within the three end-members with samples grouped between groundwater and rain end-members (Figure 3).

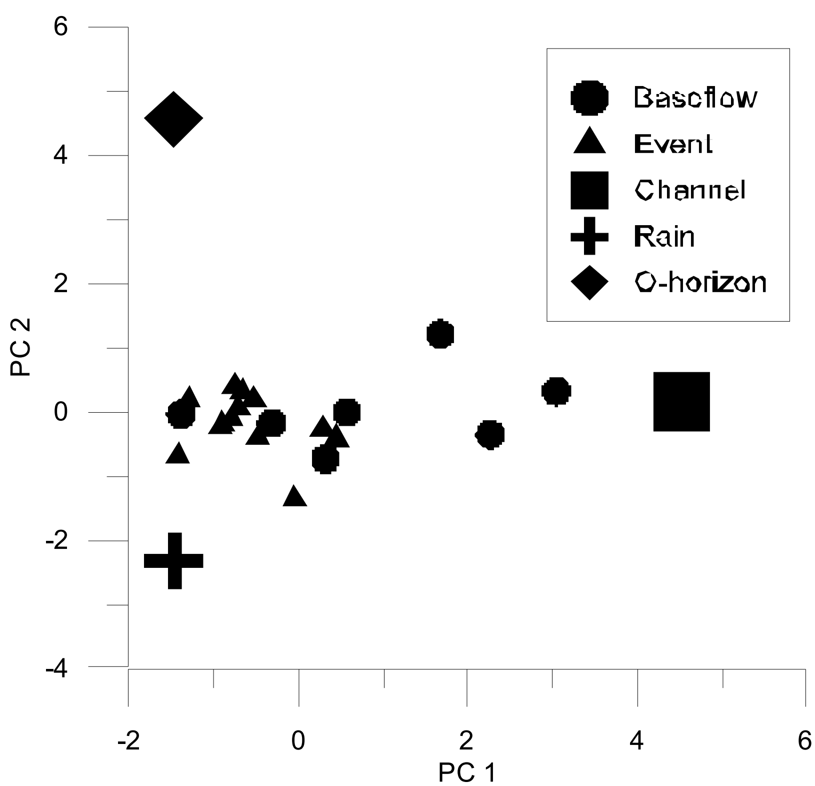


a.

Figure 3 Principle component scores of PC1 and PC2 for stream and end-member samples by watershed, (a. UC1), (b.UC2), (c.UC3), (d.UC4), and (e. UCP) from data collected at the Union Church headwater research in Webster County, Mississippi between February 2010 and May 2011

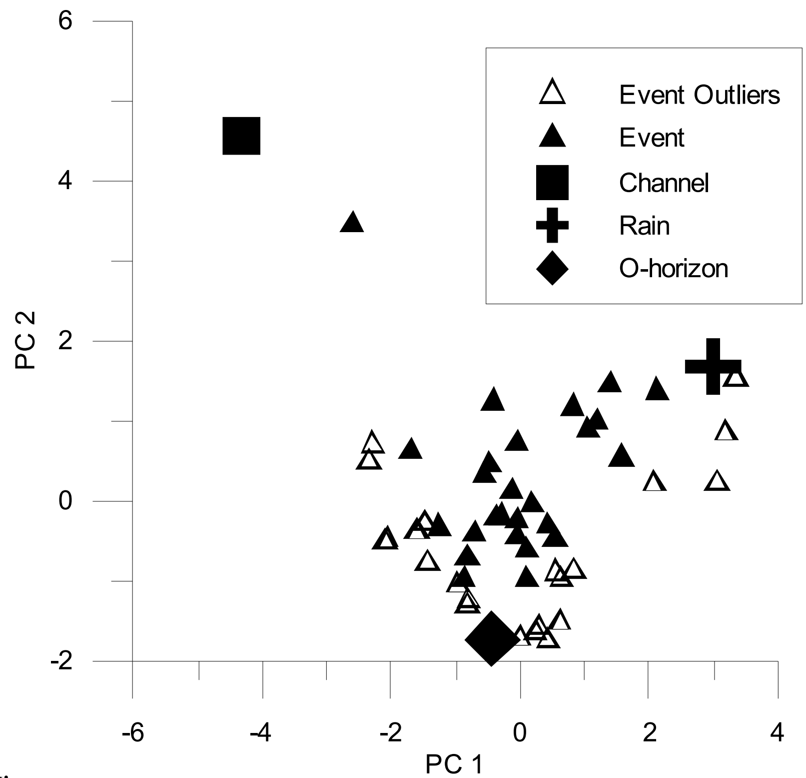


b.

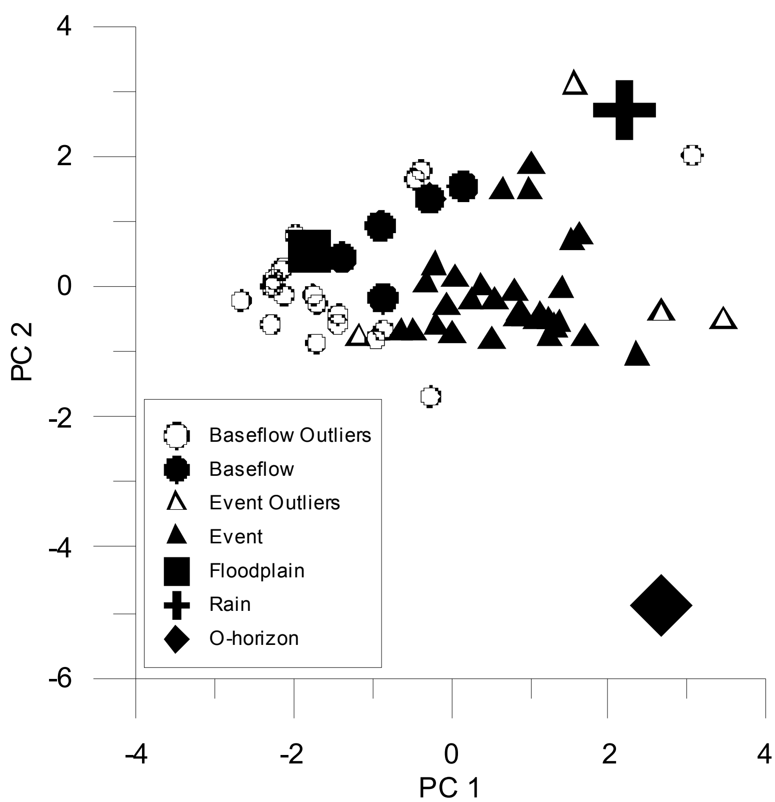


c.

Figure 3. (continued)



d.



e.

Figure 3. (continued)

The dominant source of water during events in the ephemeral and intermittent streams was rain with O-horizon making up a large proportion. The O-horizon accounted for 50% of all storm event source at UC4, while it accounted for less than 38% at the other ephemeral and intermittent streams. At UC1 O-horizon made up only slightly more (38%) source proportion than other sources. Rain dominated the source of water of UC3 (47%), but accounted for less than 37% at the other watersheds. Rain was also the main source of water at UC2 making up 41% of all event source. The source of water ranges from 20-50% O-horizon, 31-47% rain, and 18-41% groundwater at the ephemeral and intermittent streams. Groundwater was a dominant source of water during events in UC2 (41%), but accounted for less than 33% of the water from the other ephemeral and intermittent watersheds. Groundwater was the major source of water over events in the perennial stream. Baseflow discharged by the perennial and intermittent streams was similar with nearly 75% of the water originating from groundwater (Table 12). The source of water during baseflow was quite variable in the ephemeral and intermittent streams, but in general was not different from the perennial stream.

Table 12 Proportion of baseflow and event source at Union Church headwater research area in Webster County, Mississippi from data collected between February 2010 to May 2011

	Sample type		Average baseflow source			Average event source		
Site	Base-flow	Event	Ground-water	Rain	O-horizon	Ground-water	Rain	O-horizon
UC1	64%	36%	80%	8%	12%	31%	31%	38%
UC2	46%	54%	70%	17%	13%	41%	37%	22%
UC3	1%	99%	69%	22%	9%	33%	47%	20%
UC4	0%	100%	*	*	*	18%	32%	50%
UCP	75%	25%	75%	16%	9%	48%	33%	19%

* No baseflow at UC4

Groundwater contributed a larger portion to perennial stream flow than ephemeral and intermittent stream flow during events. The perennial stream had a lower average contribution from rain and O-horizon than the sub-watersheds while the intermittent and ephemeral streams had a higher contribution from rain and O-horizon than the perennial stream. During events upland sub-watersheds were more influenced by shallow lateral flow and less connected to groundwater while the reverse was true for the perennial stream.

The source of water was dynamic within each storm (Figures 4 and 5). On the rising and falling limb there appeared to be a small spike in groundwater source contribution in all stream types. The source of water from the ephemeral and intermittent streams was dominated by rain and the O-horizon. At the peak of the hydrograph O-horizon and rain were the dominant sources of water in ephemeral and intermittent streams with little influence from groundwater (Figure 4). At the beginning of events the major source of water in the perennial stream was rain with small contributions from O-horizon and floodplain groundwater. As the event progressed groundwater became a dominant source of water. In the perennial stream there appears to be a positive relationship between discharge and groundwater source of water (Figure 5).

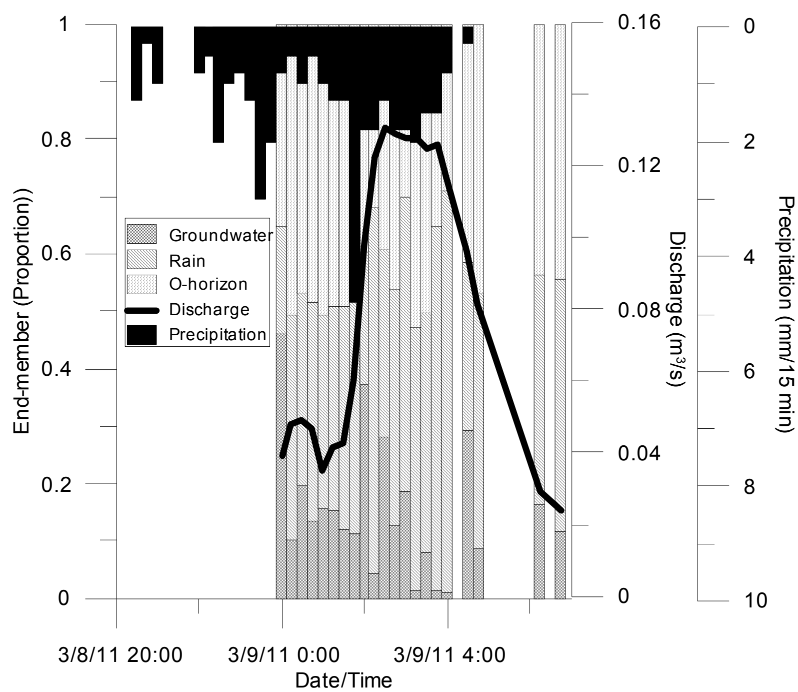


Figure 4 Precipitation, discharge, and stream sample source, over an event at UC1 located in Webster County, Mississippi during an event on March 8th 2011

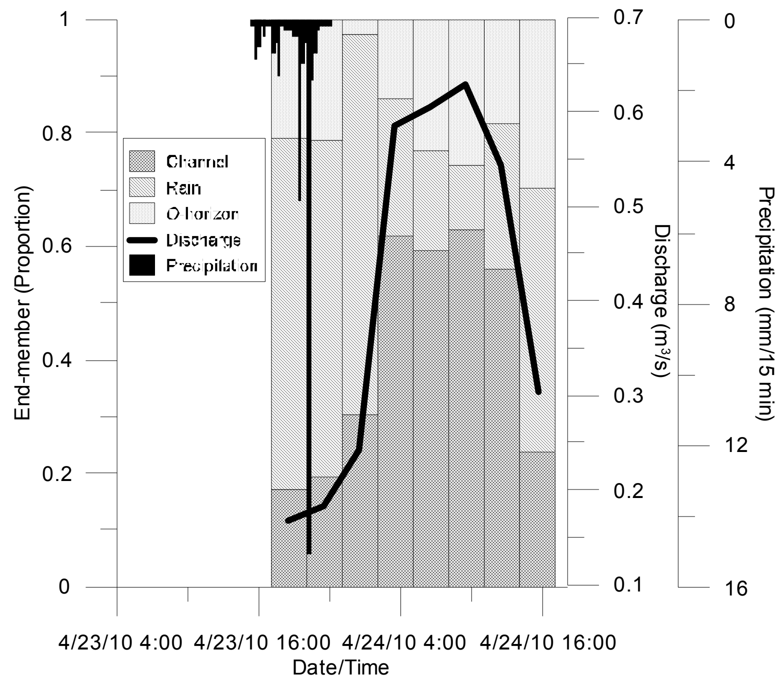


Figure 5 Precipitation, discharge, and stream sample source, over an event at UCP located in Webster County, Mississippi during an event on April 24th 2010

The source of water not only changed during the course of an event it also changed over the seasons. There were distinct differences between the response of perennial and intermittent/ephemeral streams to the change in seasons. In the intermittent/ephemeral stream (UC3) the overall source of water appears to be dominated by shallow lateral flow and rain/throughfall in April and from deeper sources (e.g. groundwater) in February (Figure 6). As the water year progressed the contribution of groundwater to intermittent and ephemeral stream flow decreased with event time. The opposite was true in the perennial stream with groundwater having more influence on the event water source as the water year progressed. There were a total of six events captured per site (Figure 7). The relationship of groundwater and water year in the intermittent and ephemeral streams has a negative relationship with a Pearson correlation of -0.93 and a p-value of 0.007. In contrast the relationship of groundwater and water year dates had a positive relationship in the perennial stream with a Pearson correlation of 0.95 and a p-value of 0.004.

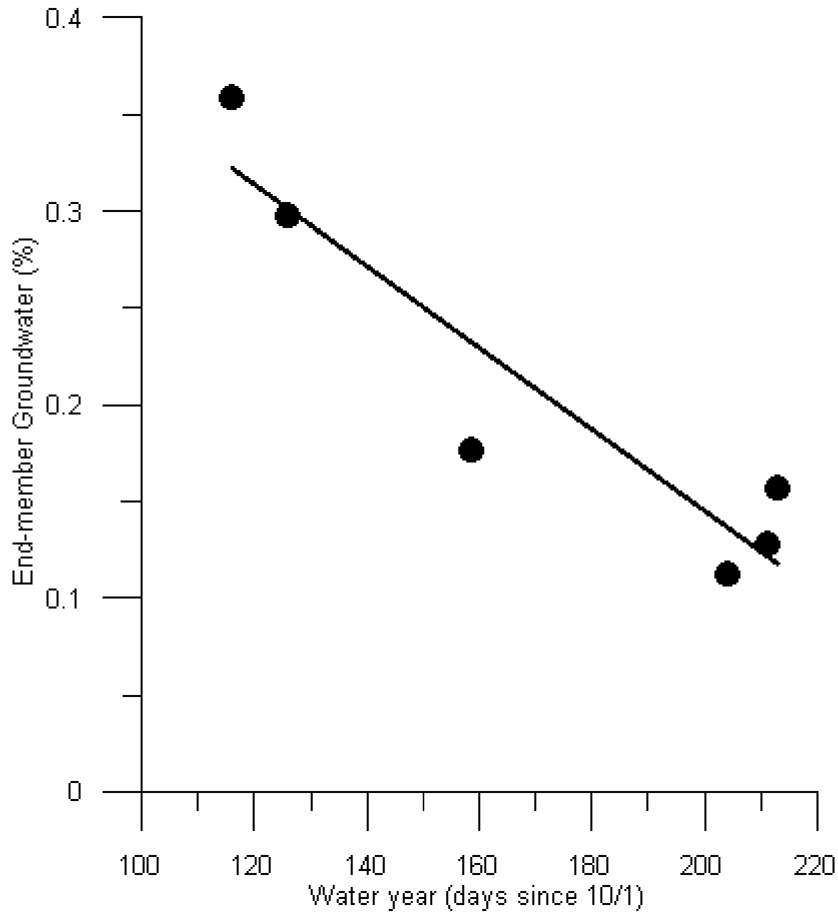


Figure 6 All event samples at UC3 with groundwater end-member values average by event, end-member channel influence on source, in relation to water year for samples collected at the Union Church headwater research area in Webster County, Mississippi

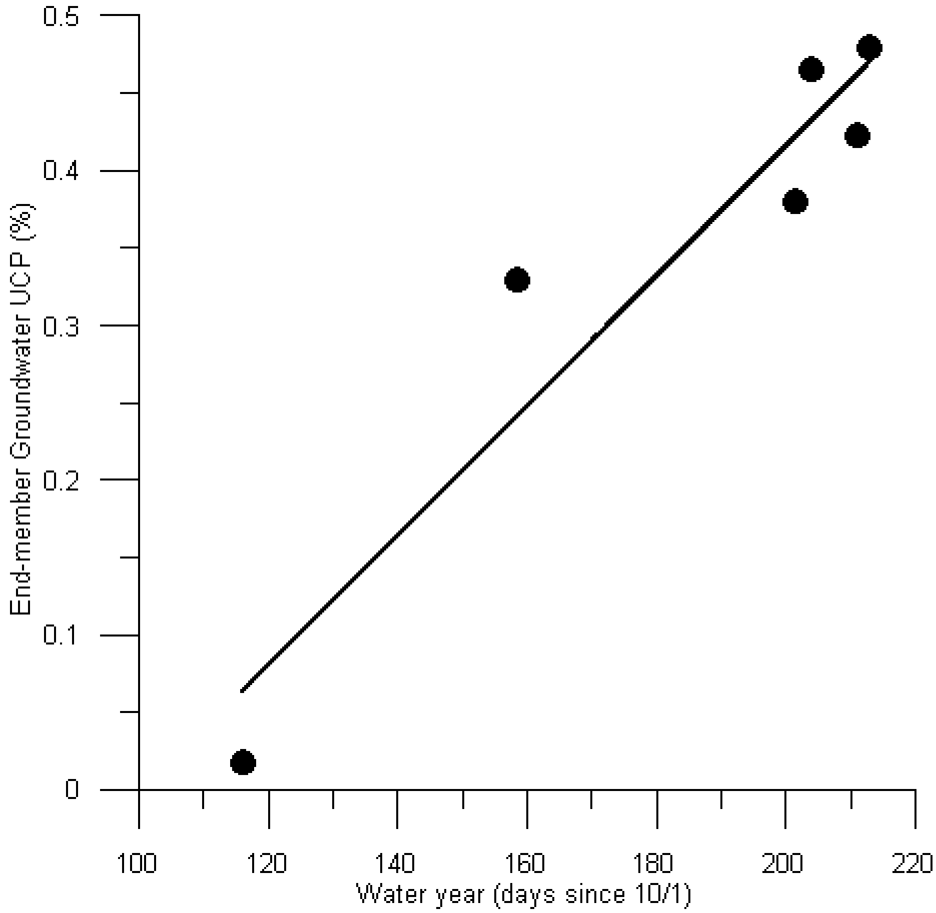


Figure 7 All event samples collected at UCP with groundwater end-member values average by event, end -member channel influence on source, relation to water year for samples collected at the Union Church headwater research area in Webster County, Mississippi

The cause of this shift in the contribution of groundwater was probably a result of a change in groundwater depth over the water year. The water table was highest from December to April and lowest from June to October with a fluctuation between dry and wet season of 160 cm measured over three year in a previous study on this site (B. Choi, unpublished data). Between late April and June (the onset of the dry season) the water table dropped substantially and remained low (200-220 cm) until late October to September, as conditions become drier the deeper groundwater resides having less influence during events. In the perennial stream ground water was closer to the surface over the course of a year contributing to perennial flow. Dry conditions in the headwater streams affected the water table depth and ultimately source. The source of water varied greatly between events and baseflow and these changes had an influence on nutrient load.

Nutrient flux and sources are intrinsically related with high nutrient flux coming from water derived from areas of high constituent concentration. With lowest constituent concentrations in groundwater and highest constituent concentration coming from the O-horizon the path water travels influences flux. With low discharge and ground water as the dominant source of water during base flow the flux is low. During events the source of water is highly variable with more influence from the O-horizon compounded by high discharge resulting in a larger nutrient flux. The time of sampling can have a large impact on nutrient concentration and can play a large role in understanding the system.

CHAPTER IV

DISCUSSION

Flux

Fluxes of dissolved constituents including nitrogen, phosphorus, and carbon are driven by soil type, precipitation, topography, and cover type among others factors (Green et al., 2007; Lewis et al. 1999; Sidle et al., 2000 ; Wipfli et al., 2007). In forested settings these factors include cover type and age, fertilizer rates, soil type, slope, climate and implemented BMPs among others. Forestry and urban areas contribute approximately 30% of the total nitrogen and phosphorus load to the Gulf of Mexico (USEPA, 2009). The median EPA estimates for total nitrogen yield for forested watersheds in ecoregion 65 is 2.02 kg $ha^{-1}yr^{-1}$. This study found total nitrogen yield (DIN +DON with the exception of PN) from the perennial stream to be 11.105 kg $ha^{-1}yr^{-1}$. This value is much larger than the EPA's estimation.

The EPA estimates phosphorus yield for forested watersheds in ecoregion 65 is 0.11 kg $ha^{-1}yr^{-1}$. This study found nutrient loss from the perennial stream of PO_4^{-3} to be 0.65 kg $ha^{-1}yr^{-1}$. Part of this discrepancy could be explained by past land use, lack of measurements, sampling methods, and the high variability inherent with headwater streams. Dissolved inorganic phosphorus is the form of phosphate required by plants for growth, and potentially the most bioavailable form for aquatic organisms.

The major form of nitrogen from this study was DON. Dissolved organic nitrogen can account for 20% to 90% of the total nitrogen load to estuaries (Seitzinger and Sanders, 1997). Lewis et al. (1999) found that the average DIN flux from temperate areas was 0.02 kg ha^{-1} yr^{-1}, with no data for DON, while fluxes of DIN and DON from tropical areas was 2.5 and 2.4 kg ha^{-1} yr^{-1} respectively. In our study we found a much larger DON flux of 10.1 kg ha^{-1} yr^{-1}. A possible reason for this difference was that this study was in a very small headwater while Lewis et al. (1999) focused on much larger watersheds and streams. As stream sizes change in stream processes also change. In stream process such as mineralization of DON to DIN, uptake by organisms and DON changing forms (e.g. DON sorbing onto sediment particles) are all processes that can reduce the proportion of DON in stream water.

Carroll et al. (2004) was the most comparable water quality study to this one. Both studies occurred in north central Mississippi in watersheds with active forest management. However, there were many differences in sampling methods between the studies. Carroll et al. (2004) utilized grab samples that were collected biweekly, syringe filtered and analyzed for dissolved NO_3^--N and other constituents. Their sample method was biased by baseflow due to the sampling method. By examining my data set I was able to calculate a biased (e.g. raw averages) by averaging the calculated concentration and an unbiased average concentration by flux (e.g. discharge) as a discharge weighted average.

Their sampling method led to the NO_3^--N concentrations of the intermittent and ephemeral streams to be underestimated between 1.39 and 3.79 times and the perennial stream was underestimated by 2.05 times. Additionally, Carroll et al. (2004) focused on dissolved nitrate while our study found that 82% - 84% of all dissolved nitrogen was organic, further underestimating dissolved nitrogen flux from these small streams. These results point to complications not accounted for in previous studies of harvesting effects on water quality. However, it should be noted the NO_3^--N concentrations in this and the Carroll et al. (2004) study were very low, so even if NO_3^--N was doubled it would not amount to a concentration or flux that would approach the magnitude discharged by other systems.

Source

The source of water in streams changes as events progress. At the beginning of an event the source of water was evenly distributed among rain, shallow lateral flow, and groundwater for the perennial stream. At the peak of the hydrograph shallow lateral flow becomes dominant in the ephemeral streams while groundwater appears to dominate the perennial streams as a result of a higher water table. Interestingly, rain becomes a dominant source of water in both streams on the falling limb. This finding is unusual because the rain has ceased by that point in the hydrograph. It is unlikely that rainfall infiltrating the soil can reach the stream without being chemically altered (Brown et al., 1999). This suggests that there is a source of water very similar to rainfall contributing to flow, possibly as a result of soil piping (Burns et al., 2001).

The source of water was driven by multiple factors such as storm intensity, and water year day which plays an important role in antecedent moisture. Green et al. (2007) examined a paired first-order agricultural watersheds and found a decreasing proportion of groundwater contributing to stormflow with increasing discharge. Research by Burns et al. (2001) in Georgia on a 10 ha catchment shows that riparian groundwater runoff was the largest component of total stream runoff with values of 80% to 100%. Research conducted by Brown et al. (1999) in New York on larger watersheds, had maximum contributions from throughfall and shallow subsurface flow with values of 46% to 75% respectively for event samples. The primary difference between my study and others was the size of the watersheds since this study was 32 ha of zero order streams and one first order stream, while the others Brown et al. (1999), Burns et al. (2001), and Green et al. (2007) studied first order streams that were all considerably larger ranging in sizes between 8 to 161 ha. Within our study scale affected the source of water by becoming more influenced by groundwater and less influenced by shallow lateral flow and rain from the headwaters to the perennial stream outlet. There appears to be a large degree of variability between systems as a result of slope, soil type, and cover type. Furthermore, the Coastal Plain has not been well studied with regard to water source, and is an area where more research needs to occur.

The source of water plays a critical role in nutrient flux. The ephemeral watershed UC4 best illustrates this point. UC4 had the highest NO_3^--N and DOC means during events. Event samples collected from UC4 were most influenced by the O-horizon end-member, possibly due to a high water table due to low evapotranspiration as a result of 100% clear-felling of the watershed 3 years prior to this study. The source of other watersheds event samples were more influenced by rain and groundwater suggesting that more of the water being discharged by UC4 is being routed through these high carbon and nitrogen soil.

Trends between watersheds

The ephemeral and intermittent streams examined in this study exhibited a wide range of natural variability with regard to flux of dissolved constituents as is expected from low order streams (Carroll et al., 2004). Since 64% of UCP's watershed had a similar stand structure to UC1 these two watersheds may have behaved similarly. Sub-watershed UC2 had the lowest flux of all constituents, possibly due to the prevalence of soil pipes within the watershed or the heavy vegetation at the site. At UC3 the streambed was highly channelized possibly affecting chemical flux. At UC4 events were flashier and lag time was significantly related to constituent yield. While these watersheds differ from one another there are many influences on yield from diffuse sources.

UCP was 11 times larger and the average maximum discharge was 27 times larger than that of the sub-catchments. This suggests that all water entering the perennial from the ephemeral/intermittent streams during large events is moving out of UCP quickly. This also suggests that during events constituents have very little time to be chemically altered. While UCP is 11 times larger than the sub-catchments it only produces 6 times more total water discharge on average. This is possibly attributed to the unmonitored large forested catchment 12.44 ha having a high evapotranspiration rates reducing the water flux during the less active portions of the hydrograph (i.e. baseflow, falling limb). This indicates that water in the perennial could become more concentrated in constituents than partially harvested sites with less evapotranspiration. I found minor trends in constituent flux from the ephemeral to the perennial scale suggesting that there is apparently enough time for some chemical alteration. Over all there is less water and constituents exiting the perennial stream than would be expected from examining the ephemerals/intermittent and how they represent the area.

Implications

By managing the source of nutrients on headwaters systems we may be able to preserve water quality. Many different silvicultural practices are being implemented on headwaters in Mississippi, all of which affect water quality to varying degrees. These areas are the sources of water and dissolved material to downstream environments. Inorganic and organic forms of nutrients such as nitrogen are constituents that frequently lead to impaired rivers in Mississippi. In forested areas there is substantially less human activity resulting in less nutrient movement. However, we found that previous studies of harvesting effects in this region have underestimated dissolved nitrogen flux by 2.05 times as a result of biased sampling and not taking into account DON. While this study cannot determine whether harvesting may or may not impact dissolved nitrogen flux it does call into questions the conclusions of the previous study (Carroll et al., 2004). In forested areas, management activities include site prep, thinning, and harvesting all have an impact on water quality. The impact of these extant physical factors on constituent loss from headwater areas can be measured, predicted, and acted upon with some degree of accuracy, particularly when the mechanisms of nutrient mobilization are understood. More research on the effects of harvesting and site preparation need to be conducted on the Coastal Plain with events and the routing of water in mind.

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