**Transport and Transformation of Nutrients and Sediment in Two Agricultural Watersheds
in Northeast Arkansas**

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Abstract

Understanding pollutant transport at different spatial and temporal scales is crucial to agroecosystems management and planning. This study aimed to reduce the knowledge gap between edge-of-field and larger agricultural watersheds. Nutrients and sediment transport and transformation at two small agricultural watersheds, Little River Ditches Basin (LRDB) and Lower St. Francis Basin (LSFB), in Northeast Arkansas, were evaluated. Flow, nutrients, and sediment were measured at 3-5 instream locations in these two contrasting watersheds. These watersheds differed in primary crop, soil type, and size.

Differences in sediment and nutrients loads were measured between the two watersheds primarily due to differences in cropping practices and soil type. LSFB was dominated by rice farms and had more pollutant load per unit area but lower concentrations for all measured parameters except nitrate, whereas LRDB was dominated by cotton farms and had less pollutant load per unit area but higher concentrations. Turbidity increased considerably at LSFB, but it did not increase or decrease at LRDB as water traveled downstream. The median nitrate-N concentration at LRDB increased from 1.64 to 2.34 mg L⁻¹ as watershed size increased, in contrast to no increase at LSFB. Total phosphorus (TP) and soluble reactive phosphorus (SRP) concentrations remained constant, but ammonium-N decreased as the water traveled downstream in both watersheds. Nitrate-N were high in spring and late fall at both watersheds. The annual loss of nitrate-N was 9.6 and 8.6 kg ha⁻¹, sediment was 1604 and 1958 kg ha⁻¹, and SRP was 0.8 and 0.9 kg ha⁻¹, respectively from LRDB and LSFB. Source control in spring and late fall could be more effective in reducing agricultural pollution.

Keywords: non-point source pollution, agricultural drainage ditch, surface water quality, nitrogen, phosphorus and sediment load, nutrients and sediment load.

1. Introduction

Non-point source pollution due to agriculture is the leading source of water quality impairment in U.S. water resources (USEPA, 1996, 2009). Poor water quality due to non-point source pollution adversely affects aquatic, human health, and economic health. The effects include excessive growth of algae, planktons and macrophytes, oxygen depletion in water, loss of fish and other species, bad taste and odor, increase in turbidity, change in temperature, increase in treatment cost for drinking water, and decrease in aesthetics/tourism and economic value of water (Carpenter *et al.*, 1998; Rabalais *et al.*, 2002). Therefore, agricultural non-point pollution control is crucial to protect the nation's water.

The Mississippi River watershed is the third largest in the world, largest in the USA and one of three most productive zones on the planet. It provides drinking water for 18 million people, produces 92% of the country's agricultural exports, and supports 180 fish species unique to the river (LMRRA, 2015). Economically, the watershed creates \$105 billion worth GDP and supports 2 million jobs directly and indirectly (LMRRA, 2015).

Hypoxia in the Gulf of Mexico due to nutrient loading from the Mississippi River watershed is well documented. Non-point source pollution from agriculture and urban activities are primary contributors to the hypoxic zone in the Gulf of Mexico and local waterways (Rabalais *et al.*, 2002). Non-point sources contribute to 78% (42% from fertilizer) of nitrogen and 66% of phosphorus loads to the Gulf of Mexico (MWNTF, 2015). The hypoxic zone in the Gulf of Mexico is the largest in the USA covering as large as 22,007 km² in 2002 (MWNTF, 2015; NOAA, 2015). Recognizing the extent and magnitude of the problem, the multi-agency Hypoxia Task Force (HTF) has set the revised goal. This goal includes a decrease of nitrogen and

phosphorus loading by 20% of the average loading from 1980 to 1996 by 2025 and decrease of the hypoxic extent to less than 5000 km² by 2035 (LMRRA, 2015).

The Delta Region of Arkansas, a major agricultural area within Mississippi River Basin, produces a major quantity of row crops annually due to a combination of fertile alluvial soil, favorable land slope, shallow groundwater, and humid subtropical climate. The high production of crops in the region contributes to high national rankings among the states in the US. In 2013, Arkansas was ranked in the top 25 states in the production of 23 commodities that included rice (#1), cotton seed (#4), sorghum (#5), and soybean (#9) (UASDA, 2014). Consequently, agriculture contributed \$20.1 billion to the Arkansas economy which is double the national average contribution to state GDP. Agriculture provided 280,959 jobs or one in six jobs and contributed 17% of the state's labor income (UASDA, 2014).

Due to the shallow water table of the Mississippi River Valley Alluvial Aquifer (MRVAA), groundwater has been increasingly used for irrigation and the estimated pumping has increased by 115% between 1985 and 2010 (Schrader, 2015). Irrigation and rainfall, in excess of infiltration, contribute to runoff events. Sediment, dissolved and adsorbed nutrients and pesticides leave the field with runoff water to drainage ditches, streams, Mississippi River, and finally to the Gulf of Mexico.

Gulf of Mexico HTF and Lower Mississippi River Conservation Committee have identified tributaries as the largest source of nutrients and sediment to the Mississippi River (LMRRA, 2015; MWNTF, 2015). They also cited the need for improved understanding of water quality and quantity at different spatial scales to develop a watershed management plan for wildlife and fish habitat management, hypoxia reduction and water quality improvement for recreation (LMRRA, 2015; MWNTF, 2015). Additionally, understanding of seasonal nutrient loadings is

important as spring (Apr-Jun) load was recently found to be highly correlated to the increase of hypoxic zone area (MWNTF, 2008). Systematic and consistent monitoring is also required to choose the optimal resource management strategies in a watershed.

Multiple agencies are working together to improve understanding of sediment and nutrient loss from fields, and their transport and transformation across various scales of agricultural landscapes. The Mississippi River Basin Healthy Watersheds Initiative (MRBI) is one of the USDA-NRCS programs that monitors nutrients and sediment at the field scale (USDA-NRCS, 2009). However, there are no studies in the region that link edge-of-field (EOF) to patterns in larger watersheds. More specifically, there are no studies in the lower Mississippi River Basin that study nutrient and sediment transport at a small watershed scale. Additionally, lower order watersheds may have features such as riparian vegetation that could aid sedimentation and treatment by reducing velocity and increasing the retention time of water. The overall effect of the processes along the first or second order streams (often present as agricultural ditches) at different cross-sections needs further study.

Therefore, we examined the nutrients and sediment in two small agricultural watersheds in Northeast Arkansas with a goal of better understanding their transport and transformation along the streams (here ditches). The two watersheds differed in size, dominant crop type, and soil. The specific objectives were to:

- I. Assess spatial variation in nitrate, ammonium, phosphorus and sediment along the stream and evaluate their transport and transformation in both watersheds,
- II. Quantify monthly and seasonal trends in nitrate, ammonium, phosphorus and sediment in each watershed, and

III. Compare two agricultural watersheds based on the flux of nitrate, ammonium, phosphorus, and sediment.

2. Methods

2.1. Study Sites

Two predominantly agricultural watersheds with different cropping practices and soil [Figure 1] were chosen for the study. The watersheds complement an ongoing field level study that measures nutrients and sediment at an EOF as part of a large state-wide MRBI network (Reba *et al.*, 2013). The two watersheds, Little River Ditches Basin (LRDB) in Mississippi County and Lower St. Francis Basin (LSFB) in Poinsett County, each had five instream water quality monitoring stations [Figure 1]. The 30-year (1981-2010) annual mean precipitation near the basins obtained from the National Oceanic and Atmospheric Administration was 1277 mm.

Along LRDB, the stations at the mainstream were named W1, W5, and W9 for downstream, midstream and upstream location, respectively [Figure 1]. W3 and W7 were located on the primary tributary streams that drained to the mainstream. The size of the basin was 53.4 km² (13,200 acres). Land use in LRDB, according to National Land Cover Dataset in 2011, was greater than 87% area in row crops, primarily soybean, and cotton. The soil in LRDB according to USDA Web Soil Survey accessed on 09/28/2015 consisted of approximately 62.0% of the area with Routon-Dundee-Crevasse complex (silt loam), 14.1% with Tiptonville and Dubbs or Dundee silt loams, 7% with Dundee-Dubbs-Crevasse complex, 6.1% with Steele and Tunica soils, and 10.8% with others. Soil hydrologic groups included C/D (64.5%), C (21.2%), A (12.4%) and D (1.8%).

Along LSFB, the stations at the mainstream were named M2, M8, and M10 for downstream, midstream and upstream location, respectively [Figure 1]. M4 and M6 were located on the tributary streams that drained to the mainstream from the EOF fields. The size of the basin was 23.35 km² (5769 acres). Land use in LSFB, according to National Land Cover Dataset in 2011, was greater than 94% of the area in row crops, primarily rice and soybean. The soil in LSFB according to USDA Web Soil Survey accessed on 09/28/2015 consisted of approximately 62.2% of the area with Sharkey-Steele complex (Clay), 29.9% with Sharkey clay, and 7.9% others. Soil hydrologic groups included D (97.4%), C/D (2.2%), C (0.2%) and A (0.3%).

LRDB and LSFB have urban areas of approximately 10.86% and 5.17% of total area, respectively. Urban sewage and wastewater produced by approximately 3,300 residents inside LRDB are collected and treated at a lagoon in the watershed. However, the effluent is disposed to water resources outside of the watershed [Personal Communication, January 2016]. Therefore, flow at the instream stations in LRDB includes only stormwater from the urban area. At LSFB, approximately five households reside within the watershed, and there is no centralized wastewater treatment system. Direct human influence on stream water other than from agricultural activities at LSFB is unlikely.

Mostly cotton-soybean rotation at LRDB and rice-soybean rotation at LSFB is in practice. Also, corn, grain sorghum and wheat are planted in a few fields each year. Conventional tillage practice is widespread in both watersheds. In both watersheds, approximately 100% of croplands are irrigated either by flooding/multiple inlet or sprinkler/pivot irrigation utilizing shallow alluvial aquifer as the source water. The fields drain via surface runoff to the ditch, and no subsurface drainage is in practice in the region. Fertilizers in the crop fields were applied according to LGU (Land Grant University) recommendations [Table 1]. All fertilizer

recommendations begin with an analysis of field-specific soil test results. Site-specific recommendations are then modified based on previous crop or soil type or a combination of both (Barber and McClelland, 2012; Hardke *et al.*, 2014; Kelley and Lawson, 2014; Ross *et al.*, 2014; Kelley and Lawson, 2015; Kelley *et al.*, 2016). At the EOF fields, P fertilizer was applied once every 2-4 years at the rate of 22-33 kg ha⁻¹ (20-30 lb acre⁻¹) [unpublished data].

2.2. Sensors and Instrumentation

Rainfall data were measured utilizing raingages stationed inside each watershed. Continuous (every 15 min) flow depth and velocity were measured in the mainstream stations except M8 using pressure transducers (Teledyne Isco 2150 AV sensor). At stations on the tributary streams (W3, W7, M4, M6) and M8, pressure transducers (In-Situ Inc. Rugged Troll 100) were used to measure flow depth. A flow rating curve developed using a portable flowmeter (Marsh McBirney Inc. Flo-Mate 2000) was used to calculate discharge.

Nutrients in the instream locations were measured using a combination of laboratory analysis and multi-parameter sondes. Turbidity, nitrate, and ammonium were monitored every 15-minutes using multi-parameter sondes (Hydrolab DS5X). Sondes were calibrated every two weeks during the growing season and three-week during the non-growing season due to issues including frequent fouling during summer and sediment/debris accumulation during large runoff events. Sondes were calibrated in the laboratory and returned to the stream in 1-2 days. Sonde deployment at stations M4 and M6 was not possible due to no flow except after big rainfall events. At upstream and downstream locations (W1, W9, M2, M10), sondes were deployed during Apr-Dec, 2015. At other locations (W3, W5, W7, M8), sondes were deployed during the growing season (May-Sep).

Continuous data acquisition was not always possible from sondes due to issues including power failure, sensor failure, and sediment and debris buildup. Corresponding unreasonable turbidity, nitrate, and ammonium values (for example, 0.0 mg L⁻¹, 3000 mg L⁻¹, *, or greater than 50 times mean) were removed before further analysis. Negative readings of the area-velocity sensor due to negligible stream velocity was replaced by zero. Continuous 15-min data were converted to an hourly average which was used to calculate daily flow-weighted mean concentrations (FWMC) [Equation 1] for turbidity, nitrate and ammonium.

$$FWMC = \frac{\sum(c_i * t_i * q_i)}{\sum(t_i * q_i)} \quad \text{Equation 1}$$

Where, c_i =concentration for i^{th} sample, t_i = time, 1 hr, q_i =discharge for i^{th} sample

2.3. Sampling and laboratory analysis

Water samples were collected weekly by automatic samplers (Teledyne Isco 6712) at five stations (W1, W5, W9, M2, M10) and manually sampled from other stations, and brought to an EPA certified laboratory at Arkansas State University. The water samples were analyzed for soluble reactive phosphate (SRP) using Method EPA 365.1; 4500-PI, total phosphorus (TP) using Method EPA 365.4; 4500-PJ and suspended sediment concentration (SSC) using Method D3977-97 (ASTM D3977-97, 1997; American Public Health Association. *et al.*, 2005).

Missing rainfall at LRDB was corrected using data from Cardwell, Dunklin County, Missouri (www.agebb.missouri.edu) after verifying the data with Cardwell Station (13 miles) and Keiser Station, Mississippi County, Arkansas (Arkansas Plant Board, 16 miles). Data corrections were made for rainfall data on 2/17-2/21, 3/8 and 6/9. Whereas, rainfall at LSFB was corrected for missing values using data from Judd Hill Station, Poinsett County (weather.astate.edu) after verifying the data with Judd Hill Station (9 miles) and Keiser Station (19 miles). Data corrections

were made for rainfall data on 1/2-1/3, 1/11-1/12, 2/17, 2/21, 3/1-3/10, 3/18-3/19, 4/9-4/10, 5/30-5/31, 8/19 and 10/23-10/25.

Missing discharges were filled using the linear relationship ($R^2 > 0.93$) between discharges at the missing station and an upstream or downstream station. The relationship between continuous daily discharge and nitrate/ammonium/turbidity was used to calculate missing daily nitrate/ammonium/turbidity for each station. No filling of data for SRP and TP was done as they were weekly data. Daily mass flux (kg d^{-1}) of nitrate, ammonium and SSC (discussed below) were calculated using the discharge and FWMC. All monthly data were derived from daily data.

Daily turbidity values (NTUs) measured by sondes were correlated to SSCs from the laboratory to use as a proxy for sediment such that continuous sediment assessment was possible. A second order non-linear fit between SSCs and NTUs was used. The relationship passed the assumptions of constant variability and normality ($p = 0.35-0.56$), the test statistic was significant ($p < 0.001$), and R^2 was 0.65 for LSFB and 0.51 for LRDB. Though R^2 values were not high for the turbidity SSC relationship, conditions in the ditches likely contributed to larger variability. Particle color, size distribution and shape, organic matter content, water flow rate and depth, time of year, land use activities are sources of variability in the relationship between SSC and NTU (Down and Lehr, 2005). Because the focus was to compare at spatial scales, the NTUs were used to compare transport of pollutants across spatial scales and SSCs were used to compare sediment flux (load).

All statistical analyses were performed in SigmaPlotv13 (Systat Software, CA). All data did not meet normality criteria in Shapiro-Wilk test. Therefore, the median $\pm$ interquartile range was used to characterize data in place of using mean values and ANOVA on ranks was performed.

Multiple pairwise comparisons were made whenever the ANOVA on ranks indicated a

significance. The relationship between variables was explored by performing Spearman correlation coefficient on daily values.

3. Results and discussion

3.1. Spatial variation

3.1.1. Turbidity and sediment

Median turbidity values at W1, W3, W5, W7, and W9 were 12.3, 15.0, 12.5, 10.3, and 14.6 NTU, respectively [Figure 2]. These values were not statistically different from each other ($p=0.09$) indicating neither significant deposition nor significant channel erosion or both. The visual observation of the ditch banks and bed supported the latter as we observed evidence of significant channel erosion, bank cutting, mass sliding, and channel bed buildup. The soil at LRDB consisted of silty loams dominated by Routon-Dundee-Crevasse complex (86% in hydrologic group C or C/D) (McKimmey *et al.*, 2002). The high soil erodibility (erodibility factor=0.49) and a flat channel bed also supported our observations. At LSFB, the median turbidity values at M2, M8 and M10 were 51.3, 33.4 and 33.6 NTU, respectively. The turbidity at LSFB increased as the water traveled downstream indicating significant channel erosion and sediment transport along the ditch. Erodibility was high in the watershed as clayey soil covered over 92% of the area.

Drainage ditches/streams are designed as water conduits; however, important biogeochemical cycles of nutrients can occur in stream. Aquatic macrophytes may aid sedimentation by reducing velocity and increasing retention time and removing associated particulate pollutants from water. Though not measured, emergent vegetation at the tributary streams and submerged vegetation at mainstream stations W5 and W9 were observed qualitatively. Patches of vegetation were also present between mainstream stations. Despite the presence of vegetation, reduction of turbidity

was not observed, similar to a study where the addition of riparian vegetation and habitat with varying amounts of riparian function did not improve water quality (Stringfellow *et al.*, 2010).

Tributary ditches had shallow water depth and slower velocities, and field observations indicated more dense vegetation. These combined features likely drove longer residence time of water providing an extended opportunity for settlement of sediment and particulate pollutants than in the mainstreams. Whereas, mainstreams in this research had deeper water depth, less vegetation, more velocity (depending on location), and less retention time. Despite these differences, turbidity and SSC were similar at tributary and mainstream locations.

3.1.2. Nitrate

Nitrogen inputs in a watershed are determined by upstream human activities, climate, and processes in the ditch itself. Runoff from the fields and groundwater intrusion were likely major sources of nitrogen in both watersheds (Duff *et al.*, 2008). Other potential sources were atmospheric deposition and sediment processes (Bernot and Dodds, 2005; Strock *et al.*, 2007). These sources contributed to median nitrate-N concentrations in the mainstream of 2.34, 1.59 and 1.64 mg L⁻¹ at W1, W5, and W9, respectively [Figure 2]. Whereas, median concentrations in the tributary ditches were 1.65 and 1.26 mg L⁻¹. These values were lower than in similar streams in Maryland and Washington (2.9 mg L⁻¹) and higher than in Nebraska (0.8 mg L⁻¹) during September or May when flows were low (Duff *et al.*, 2008). Total nitrogen concentration in northeast Arkansas in a USGS national study was 0.66-3.17 mg L⁻¹ (Dubrovsky, 2010). Nitrate-N concentrations at W3 and W7 were not statistically different ($p=0.18$). However, the most downstream location had 2.34 mg L⁻¹ nitrate-N, significantly higher than concentrations at all other locations ($p<0.05$). A similar increase in nitrate-N concentration after agricultural drainage was observed by Dukes and Evans (2006) in North Carolina where the authors reported average

nitrate-N concentrations of 3.4-4.1 mg L⁻¹ (Dukes and Evans, 2006). Pasture and animal agriculture upstream of the sampling location contributed to higher nitrate-N concentrations (Dukes and Evans, 2006). In another study in Australia, nitrate concentration increased with distance in two contrasting agricultural watersheds (Connolly *et al.*, 2015). However, in yet another study, median concentration of nitrate-N did not increase or decrease as the water flowed through 428-1145 m stream sections without any surface water inflow in each section (Duff *et al.*, 2008). At LSFB, the median nitrate-N concentrations were 1.4, 1.6, 1.8 mg L⁻¹, respectively and were not different among each other despite increasing concentrations ($p=0.34$).

Nitrogen removal from a ditch section can occur by denitrification (dissimilatory reduction of nitrate or nitrite to nitrogen gas), plant uptake and harvesting/removal of biomass, ammonia volatilization and transport downstream. Plants can uptake nitrate and ammonium, and influence denitrification by providing electron donor (organic carbon) and oxygen (Schaller *et al.*, 2004). Denitrification can also occur in anoxic zones of thick algae and macrophyte mats, and benthic sediment as both systems have carbon to donate electrons (Schaller *et al.*, 2004). Water velocity determines the ability to transport pollutants directly and fate of the nutrients indirectly by influencing residence time (plant and microbial uptake), diffusion, and oxygenation (Horner and Welch, 1978; Larned and Atkinson, 1997).

In the studied streams, increase in nitrate-N concentrations along the stream network within LRDB and statistically similar nitrate-N concentrations along the stream network within LSFB were observed. W1 had the shallowest water depth, and the highest flow velocity, creating favorable conditions for oxygenation and nitrification (microbial oxidation of ammonium to nitrate and nitrite). Combined with hydrology, the nitrate flux significantly increased from upstream to downstream in both watersheds. A similar result to LSFB was obtained before (Duff

et al., 2008; Connolly *et al.*, 2015). One reason that decreases in N were not observed may be that denitrification levels were far below the magnitude of N inputs (Schaller *et al.*, 2004). As the rate of nitrogen loss declines with the increase in stream size (Alexander *et al.*, 2000), the nitrogen concentration is unlikely to decrease as the water makes its way downstream to the Mississippi River.

Entrance of nitrogen to the ditch can be prevented by in-field practices such as precision nutrient management (source, rate, timing and placement of nutrient application), irrigation management, modification of farming practices (cropping systems, using nitrification inhibitors, tillage practice, residue management, cover crops), and EOF practices such as impoundment, buffers, filters (Mitsch *et al.*, 2001; Dabney *et al.*, 2006). Alternatively, proper instream management practices such as wetlands (Hunt *et al.*, 1999; Tanner *et al.*, 2005), riparian buffers (Mitsch *et al.*, 2001), bioreactors (Hua *et al.*, 2016), artificial dam and flow path modifications (Craig *et al.*, 2008) can reduce nitrogen in the stream. For example, instream wetlands reduced nitrogen concentration by 20-70% by enhancing residence time, and providing reduced conditions and carbon (Hunt *et al.*, 1999; Tanner *et al.*, 2005; Evans *et al.*, 2007).

3.1.3. Ammonium

Median ammonium-N concentrations at W1, W5, and W9 were 0.07, 0.15, and 0.09 mg L⁻¹, respectively [Figure 2]. Ammonium-N concentrations were similar to 0.01-0.11 mg L⁻¹ obtained in Washington, Nebraska and Maryland in agricultural streams in low flows in September or May (Duff *et al.*, 2008). However, these values were lower than 0.5-0.6 mg L⁻¹ obtained in a mainstream in a North Carolina study likely elevated due to additional nutrient inputs from animal manure in the watershed (Dukes and Evans, 2006). The ammonium-N concentrations at W3 and W7 were 0.19 and 0.46 mg L⁻¹, respectively. The concentrations at W3 and W5 were

statistically similar ($p>0.05$), but higher than that at W9. Mixing of water from W7 may have contributed to higher ammonium-N concentration at W5 than at W9. The concentrations at W7 were significantly higher than concentrations at other locations ($p<0.001$) likely due to the water processes. W7 was located directly upstream of a road culvert, the outlet of which was higher than the stream bed. The higher elevation of the culvert outlet than stream bed created a permanent pool of water that acted as an artificial detention pond/wetland and likely increased ammonium-N concentration. In a similar setting, an increase in ammonium-N concentration by 0.2 mg L^{-1} was obtained as the water flowed through an instream wetland in summer (Hunt *et al.*, 1999). As the water from W3 and W5 mixed and flowed downstream, ammonium-N concentration at W1 decreased significantly ($p<0.001$). At LSFB, the median concentrations of ammonium-N were 0.23 , 0.31 , and 0.24 mg L^{-1} at M2, M8, and M10, respectively. The concentration at M8 was significantly higher than that at M2 and M10 ($p<0.001$) for the same reason as W7.

3.1.4. SRP and TP

Median SRP concentrations at LRDB were $0.16\text{-}0.17 \text{ mg L}^{-1}$ and at LSFB were $0.15\text{-}0.19 \text{ mg L}^{-1}$ [Figure 2]. They were not different among sampling sites ($p>0.05$) at both watersheds. The observed SRP concentrations were higher than those in agricultural streams in Washington (0.08 mg L^{-1}), Nebraska (0.01 mg L^{-1}) and Maryland (0.03 mg L^{-1}) during May or September (Duff *et al.*, 2008), and a stream draining dairy pasture at North Carolina (0.041 mg L^{-1}) (Dukes and Evans, 2006). These differences were likely due to a combination of factors including fertilizer and manure application, soil and climate. However, SRP concentrations in the current study, 0.16 ± 0.08 at LRDB and $0.16\pm0.08 \text{ mg L}^{-1}$ at LSFB during May-Aug were lower than $0.38\pm0.17 \text{ mg L}^{-1}$ (mean $\pm$ standard deviation) in similar sized ditches in the Northeastern Arkansas during the same period (Bouldin *et al.*, 2004).

Median concentrations of TP at W1, W3, W5, W7, and W9 were 0.31, 0.32, 0.32, 0.33, and 0.48 mg L⁻¹, respectively. Median concentrations of TP at LSFB stations were 0.34-0.38 mg L⁻¹. The concentrations were not different among each other ($p > 0.882$) at both watersheds. The TP concentrations were higher than those in agricultural streams during May or September at Washington (0.33 mg L⁻¹), Nebraska (0.01 mg L⁻¹) and Maryland (0.15 mg L⁻¹) (Duff *et al.*, 2008), and North Carolina (0.09 mg L⁻¹) (Dukes and Evans, 2006). Total phosphorus concentration in northeast Arkansas in a USGS national study was 0.05 to greater than 0.28 mg L⁻¹ (Dubrovsky, 2010).

SRP and TP concentrations were relatively constant at all stations including tributary stations, similar to a study in an agricultural watershed in Australia (Connolly *et al.*, 2015). Therefore, no reduction in SRP or TP concentration was obtained as the water moved through the stream. It was likely due to contrasting effects of instream phosphorus-loss processes and downstream phosphorus additions via runoff and groundwater intrusion (Vadas *et al.*, 2007). TP concentrations were always greater than SRP concentrations ($p < 0.03$) indicating significant presence of particulate and organic phosphorus in the water. SRP was always higher than 0.01-0.02 mg L⁻¹, the threshold for P starvation in freshwater ecosystems (Dukes and Evans, 2006). This implied that the SRP, in excess concentrations than is required for eutrophication, may travel further downstream and to the Gulf of Mexico without any reduction from watersheds like these. SRP can undergo plant uptake and assimilation, release, and adsorption/desorption to sediment and vegetation in the ditch (Stringfellow *et al.*, 2010). While stream sediments can be a source of SRP (Zamparas and Zacharias, 2014), it was possibly absent or in dynamic equilibrium in this study. Instead, SRP in the water was likely from P fertilizer or from P-rich agricultural soil that had TP concentrations of 290-430 mg L⁻¹ [Unpublished data]. Therefore, efforts aimed

at reducing the phosphorus load should consider reducing the phosphorus loss at the field or capture instream phosphorus using engineering measures including riparian buffers, grassed waterways, impoundments (settling basin) (Sharpley and Wang, 2014), wetlands (Tanner *et al.*, 2005), filters (Canga *et al.*, 2016), and PSM (phosphorus sorbing materials) structures (Penn *et al.*, 2007; Hua *et al.*, 2016).

3.2. Temporal variation

The discharge at the downstream stations W1 and M2 ranged from 0.04 to 23.07 m³ s⁻¹ (LRDB), and 0.0-5.55 m³ s⁻¹ (LSFB). The mainstream was not dry all year-round at LRDB and was dry for only a few days during the driest part of the year at LSFB. The peaks in the hydrograph were due to quick flow that resulted from rainfall events and rapid interflow, whereas, base flow in the hydrograph was due to groundwater discharge. High variability in discharge was obtained in March, November and December as the magnitude of flood greatly exceeded the median flow [Figure 3]. As expected, discharge at all stations was positively correlated with rainfall ($R^2=0.43-0.67$ ($p<0.001$)).

Turbidity followed the discharge pattern, increasing substantially in spring, November and December [Figure 3]. Sediment transport was highest during Apr-Jun, likely due to earlier tillage activities in the field, lack of plant cover, and high rainfall. Whereas during Nov-Dec, the crops were harvested and fields often tilled and barren, and high rainfall washed away sediment. Even during Nov-Dec, turbidity was low during low flow conditions. September was characterized by the lowest rainfall, discharge, and turbidity among all months monitored. In a large agricultural watershed in Louisiana, turbidity was highest during Mar-Apr and lowest in Sep (Poudel *et al.*, 2013). Site-specific daily turbidity varied from <1-1823 NTU at LRDB (N=968), and <1-928

NTU at LSFB (N=707). Minimum, mean and maximum turbidity in the similar sized ditches in the region during May-Aug were <10, 48-66, and 222 NTU, respectively (Bouldin *et al.*, 2004).

At both watersheds, nitrate-N concentrations were high ($>2 \text{ mg L}^{-1}$) during Apr-May and Nov-Dec when plant uptake was low and rainfall was high (Dukes and Evans, 2006), and low during Jun-Jul despite the fact that fertilization is mostly carried out in June [Figure 4]. Low concentration values could be due to very low rainfall in June and limited runoff from the fields. By July, plants may have utilized easily available nitrogen from fertilizer. Additionally, distinctly low concentrations of nitrate in the stream were observed during Sep-Oct only at LSFB likely due to drainage of rice fields prior to September. Nitrate-N concentration in runoff from field was lowest from rice fields compared to other crops in China (Chen *et al.*, 2016). Nitrate is present in very low concentrations in the flooded water in the rice fields due to use of ammonium-based fertilizers, low rate of nitrification ($0.013 \text{ mg N g}^{-1} \text{ day}^{-1}$) and high rate of denitrification ($5\text{-}318 \text{ mg N g}^{-1} \text{ day}^{-1}$) (Zhou *et al.*, 2012). Mean nitrate-N concentrations obtained in a tile drained, small agricultural watershed in east-central Illinois were $10\text{-}18 \text{ mg L}^{-1}$ from Feb-Jun and less than 1 mg L^{-1} from July onwards (Schaller *et al.*, 2004). Increased nitrate-N concentration in low flow of Aug-Sep at LRDB was likely due to groundwater seepage as a point source was absent. A study in three streams with diverse vegetation, channel characteristics and sediment organic matter in three states found 8-42% increases in nitrate-N loads from groundwater seepage in May or September (Duff *et al.*, 2008). The intrusion of groundwater to the stream after a wet spring was likely as the ditches were lower than the groundwater table, like in Maryland under similar soil type (Vadas *et al.*, 2007). Daily nitrate-N concentrations were higher than 10 mg L^{-1} , greater than the maximum contaminant level for drinking water (US EPA,

2016), in 57 samples at LRDB ((N=967, spring, summer, fall) and 34 samples at LSFB (N=662, mostly late fall).

Ammonium-N concentrations increased steadily until May or June depending on the site, then steadily decreased until October, and increased again in Nov-Dec [Figure 4]. In summer, ammonium concentration increased as nitrate decreased, and vice-versa, in both watersheds. Due to high air temperature in summer, ammonification of organic nitrogen occurred faster, and nitrification occurred slower due to lower dissolved oxygen (Hunt *et al.*, 1999). Due to small concentrations of ammonium-N compared to nitrate-N, nitrification of ammonium may not have affected the overall nitrate-N concentration. The removal of ammonium-N due to volatilization and nitrification was greater during winter months (Hunt *et al.*, 1999). More oxidized conditions in cooler months due to slower plant growth and respiration contributed to higher nitrification.

Monthly SRP and TP concentrations did not vary at both watersheds [Figure 5] indicating excess (greater than 0.01-0.02 mg L⁻¹) SRP presence for the entire year. At both watersheds, SRP was relatively constant from Mar-Nov and decreased in December. However, TP showed distinct peaks during some months at W9 and W3. These stations had low velocities providing longer retention time and subsequent rise in algae biomass (Yang *et al.*, 2008) that contribute to higher particulate phosphorus (Wasley, 2007).

Thus, November and December had the highest concentrations and loading of pollutants.

Consequently, prevention measures that target reduction at the source during this time period such as cover crops (Drury *et al.*, 2014), grass barriers, buffers and filter strips (Blanco-Canqui *et al.*, 2004), tail-water recovery (Sullivan and Delp, 2012), and no or minimum tillage (Smith *et al.*, 2015) may be effective. To sum up, the reduction of water and nitrogen use, and the

provision of continuous ground cover and barriers from fall to spring are important (Udawatta *et al.*, 2006).

3.3. Mass flux and transport downstream

Discharge increased with each downstream location as tributary ditches and fields drained directly to the mainstream. Consequently, an increase in mass flux (kg d^{-1}) was expected. Sediment and nitrate fluxes at the downstream were higher than at the upstream or midstream locations at both watersheds [Table 2]. This indicated that instream removal of pollutants was not significant despite the presence of vegetation and/or new discharge in between stations had significant pollutants. In a simulated storm runoff study along 320 m long vegetated and non-vegetated ditches in Mississippi Delta region, vegetation did not reduce instream nitrate, ammonium and dissolved organic phosphorus loads (Moore *et al.*, 2010) likely due to short retention time. Sediment flux was greatest at W1, followed by W5 and W9 ($p < 0.05$). Nitrate-N flux at W1 was greater than that at W5, but W5 and W7 had similar nitrate-N fluxes. Ammonium-N flux was lowest at W9, but W5 and W1 had similar fluxes. At LSFB, sediment and nitrate flux were greatest at M2, but M8 and M10 had similar sediment and nitrate fluxes. At LSFB, ammonium-N flux increased as the water from more rice fields drained and moved downstream ($M2 > M8 > M10$). SRP and TP mass flux increased as the water moved downstream, a reflection of similar concentrations at all stations, but increased discharge.

3.4. Comparison of watersheds

The watersheds were different in size, soils, agricultural coverage, crops, and stream characteristics [Table 3]. Consequently, differences in concentrations and patterns of nutrients and sediment between two watersheds were observed. At both watersheds, rainfall had significant positive relationship with discharge, turbidity and ammonium-N, and no significant

relationship with SRP and TP [Table 4]. However, nitrate-N concentration was correlated to rainfall only at the LRDB, but not at LSFB, likely associated with capture of rainfall in the rice field and controlled release of runoff.

Additionally, turbidity was significantly and positively correlated with discharge [Table 4] demonstrating that the increased discharge transported soil particles from fields to streams. However, the relationship between turbidity and discharge was stronger at LRDB (Correlation coefficient = 0.69) compared to that at LSFB (correlation coefficient=0.40). LRDB had coarser soil (silt loam) than LSFB (Sharkey clay) and was more prone to erosion. The annual median SSC was 0.43 g L^{-1} at LRDB and 0.29 g L^{-1} at LSFB. Haziness by clay particles likely contributed to greater median turbidity at LSFB (51.3 NTU) than at LRDB (12.0 NTU) despite lower SSC. Turbidity increased considerably at LSFB as the water traveled downstream, unlike in LRDB. LSFB had lower maximum turbidity despite higher median turbidity than LRDB. The annual sediment lost from LRDB and LSFB downstream stations were $1604.1 \text{ kg ha}^{-1}$ and $1958.3 \text{ kg ha}^{-1}$, respectively. Higher water yield at LSFB led to higher sediment yield at LSFB than at LRDB despite having lower SSC. Additionally, higher transport of clays than silt loams and presence of a greater ratio of agricultural area to total area likely contributed to higher sediment yield at LSFB.

Annual median nitrate-N concentration increased from upstream to downstream in the LRDB from 1.6 to 2.3 mg L^{-1} , but not in the LSFB. The Nitrate-N increase in LRDB could be due to an increase in the proportion of agricultural area downstream compared to upstream as urban area was located in the upstream at LRDB. These trends were likely determined by the processes in the stream and the rate and timing of fertilizer application in the fields that drained between upstream and downstream. Annual nitrate-N lost from LRDB and LSFB was 9.6 kg ha^{-1} and 8.6

kg ha⁻¹, respectively. The losses were similar to 8-14 kg ha⁻¹ annual nitrate-N lost from corn-soybean rotation fields of three very small watersheds (1.65-4.44 ha) consisting of silt loam soil above clay pan in Missouri (Udawatta *et al.*, 2006).

Ammonium-N concentrations ranged from 0.07-0.46 mg L⁻¹ and decreased at the downstream compared to upstream or midstream in both watersheds [Table 3]. Ammonium concentration was higher in magnitude at LSFB than at LRDB likely associated to rice cropping. Application of ammonium fertilizers, limited rate of nitrification and slow ammonification rate of organic nitrogen contribute to ammonium accumulation in rice fields (Ishii *et al.*, 2011). Annual ammonium-N lost from LRDB and LSFB were 0.3 kg ha⁻¹ and 1.2 kg ha⁻¹, respectively.

Increased nitrate-N and ammonium-N concentrations in the water were correlated to increased discharge [Table 4]. Runoff from more farms and possibly groundwater intrusion led to more concentration than dilution of water thus elevating the concentrations of nitrate and ammonium. On the overall basis, nitrate and ammonium increased together at both watersheds as they were positively correlated. However, in the summer, increase in nitrate was characterized by decrease in ammonium.

SRP and TP remained uniform as the water flowed downstream at both watersheds. Annual SRP and TP lost from LRDB were 0.8 and 1.2 kg ha⁻¹, and from LSFB were 0.9 kg ha⁻¹ and 2.1 kg ha⁻¹, respectively. SRP concentration was negatively correlated to discharge only at LRDB, whereas, total phosphorus was positively correlated to discharge only at LSFB [Table 4]. At both watersheds, SRP and TP were not correlated to turbidity indicating particulate phosphorus associated with sediment load was not a major source of phosphorus.

3.5. Conclusions

This study included continuous data on nitrate, ammonium and turbidity, and weekly data on phosphorus and sediment at several locations along longitudinal sections of first or second order streams (agricultural drainage ditches) in two small agricultural watersheds in Northeast Arkansas. This study aimed to fill the gap in nutrients and sediment dynamics between field scale and large watershed scale studies. SSC concentration from LRDB (cotton and soybean crops predominantly) was higher than that from LSFB (rice and soybean crops predominantly). However, total sediment yield was higher at LSFB as the watershed had primarily clay soil and yielded higher runoff per unit area than LRDB. The concentration of nitrate-N increased upstream to downstream as the water traveled along LRDB and received runoff from more farms, however, it did not increase or decrease along the stream in LSFB. Contrasting nitrate and ammonium trends were observed between the watersheds due to differences in management of major crop i.e. rice in LSFB compared to cotton in LRDB. More specifically, LRDB had higher ammonium concentration, but lower nitrate concentration than LSFB. Ammonium-N concentration was highest in the summer than other months and reduced or remained constant as water traveled downstream. There was no observable transformation of SRP or TP during instream transport. Between the two watersheds, LSFB had higher pollutant load per hectare than LRDB except for nitrate-N, again related to rice cropping at LSFB compared to cotton at LRDB. The results stress the importance of controlling nutrients and sediment at source using proper on-farm strategies targeting spring and late fall to reduce the high loads from agriculture. Additionally, engineering of potential instream mitigation practices may be necessary.

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Table 1 LGU (Land Grant University) recommendations for fertilizer and irrigation application in common row crops in Arkansas.

Crop	Rice	Soybean	Cotton	Corn	Sorghum	Wheat
Nitrogen fertilization	Urea or ammonium sulfate at 168 kg ha ⁻¹ (150 lb acre ⁻¹) either pre-flood or split (70% pre-flood and 30% mid-season	Does not apply	Urea or DAP or ammonium sulfate at 36-55 kg (80-120 lb) N acre ⁻¹ in split applications	Urea or DAP or ammonium sulfate at 180-390 kg (160-290 lb) N acre ⁻¹ in split applications	Urea or DAP or ammonium sulfate at 123-224 kg (110-200 lb) N acre ⁻¹ in split applications	Up to 207 kg (185 lb) N acre ⁻¹ in split applications based on soil texture and previous crop
Phosphorus (P₂O₅) fertilization	0-101 kg ha ⁻¹ (0-90 lb acre ⁻¹) based on soil P and pH test results	0-90 kg ha ⁻¹ (0-80 lb acre ⁻¹) based on soil P test results	0-101 kg ha ⁻¹ (0-90 lb acre ⁻¹) based on soil P test results	0-146 kg ha ⁻¹ (0-130 lb acre ⁻¹) based on soil P test results	0-123 kg ha ⁻¹ (0-110 lb acre ⁻¹) based on soil P test results	0-112 kg ha ⁻¹ (0-100 lb acre ⁻¹) based on soil P test results
Potassium (K₂O)	0-101 kg ha ⁻¹ (0-90 lb acre ⁻¹) based on soil K test results	0-90 kg ha ⁻¹ (0-80 lb acre ⁻¹) based on soil K test results	0-157 kg ha ⁻¹ (0-140 lb acre ⁻¹) based on soil K test results	0-179 kg ha ⁻¹ (0-160 lb acre ⁻¹) based on soil P test results	0-168 kg ha ⁻¹ (0-150 lb acre ⁻¹) based on soil P test results	0-157 kg ha ⁻¹ (0-140 lb acre ⁻¹) based on soil P test results
Irrigation	76 cm (30 inches) from 5 th leaf or 1 st tiller stage to 30 days before 50% saturation	51-64 cm (20-25 inches) from germination and seedling stage to when 50% of pods are at R6 stage	7-10 days after bloom to 350-450 Heat Units past cutout at 5-8 cm (2-3 inch) deficit based on soil texture	46-58 cm† (18-23 inches) from germination and seedling stage to >50% starch line movement	51 cm† (20 inches) from germination and seedling stage to >75% of heads are at hard dough	
Reference	(Hardke <i>et al.</i> , 2014)	(Ross <i>et al.</i> , 2014)	(Barber and McClelland, 2012)	(Kelley and Lawson, 2014)	(Kelley and Lawson, 2015)	(Kelley <i>et al.</i> , 2016)

† Derived from estimated water use during different growth periods

Table 2 Average monthly mass flux (kg d^{-1}) at each station at both watersheds. Values are median $\pm$ interquartile range. At least a letter common at the suffix indicates the statistical indifference. Stations are shown from downstream to upstream.

Watershed	Station	Sediment	Nitrate	Ammonium	Soluble Reactive P [†]	Total P [†]
LRDB	W1	23,120.5 $\pm$ 45,987.0 ^a	137.9 $\pm$ 327.8 ^a	4.6 $\pm$ 12.4 ^a	10.9 $\pm$ 6.2 ^a	17.9 $\pm$ 12.8 ^a
	W3	2504.4 $\pm$ 1625.5 ^b	10.4 $\pm$ 15.8 ^b	1.1 $\pm$ 1.9 ^b	0.9 $\pm$ 0.2 ^{bc}	2.3 $\pm$ 1.2 ^{bcd}
	W5	12,501.1 $\pm$ 25,133.0 ^c	37.0 $\pm$ 83.4 ^c	6.0 $\pm$ 14.5 ^a	5.7 $\pm$ 4.0 ^a	11.1 $\pm$ 9.6 ^{ac}
	W7	429.9 $\pm$ 642.0 ^d	1.2 $\pm$ 2.0 ^d	0.3 $\pm$ 0.4 ^c	0.1 $\pm$ 0.1 ^b	0.3 $\pm$ 0.3 ^b
	W9	7625.6 $\pm$ 5530.4 ^e	41.2 $\pm$ 94.9 ^c	2.0 $\pm$ 7.5 ^d	2.8 $\pm$ 1.1 ^{ac}	10.4 $\pm$ 3.4 ^{ad}
LSFB	M2	10,856.3 $\pm$ 17261.6 ^a	47.7 $\pm$ 180.1 ^a	6.4 $\pm$ 15.2 ^a	5.1 $\pm$ 7.2 ^a	11.6 $\pm$ 15.8 ^a
	M4				1.0 $\pm$ 1.5 ^{ab}	2.4 $\pm$ 3.7 ^{ab}
	M6				0.0 $\pm$ 0.0 ^b	0.0 $\pm$ 0.0 ^b
	M8	3621.8 $\pm$ 7409.3 ^b	18.0 $\pm$ 37.1 ^b	3.6 $\pm$ 7.4 ^b	1.0 $\pm$ 2.2 ^{ab}	2.3 $\pm$ 4.0 ^{ab}
	M10	1446.5 $\pm$ 3900.1 ^b	9.4 $\pm$ 33.4 ^b	1.3 $\pm$ 3.9 ^c	0.7 $\pm$ 0.4 ^{ab}	1.6 $\pm$ 1.3 ^{ab}

[†] Calculated using monthly median concentration and monthly median flow.

Table 3 Comparison of two watersheds and transport of pollutants at each watershed.

	LRDB		LSFB	
	Downstream (W1)	Upstream (W9)	Downstream (M2)	Upstream (M10)
Size, acres	13,200		5769	
Major Soil	Routon-Dundee-Crevasse complex (silt loam)		Sharkey-Steele complex (clay)	
Soil hydrologic group	C/D (64.5%), C (21.2%), A (12.4%)		D (97.4%), C/D (2.2%)	
% Agricultural	87		94	
Crops	Cotton, soybean		Rice, soybean	
Ditch characteristics (tree canopy, width, depth)	No riparian trees, straight stream section, wide		Riparian trees between M10 and M2, meandering, narrow	
Rainfall in 2015 (mm)	1517		1480	
Maximum runoff ($\text{m}^3 \text{s}^{-1}$)	23.07	4.18	5.5	5.17
Median runoff ($\text{m}^3 \text{s}^{-1}$)	0.7	0.2	0.3	0.1
Median nitrate (mg L^{-1})	2.3	1.6	1.4	1.8
Median nitrate (kg d^{-1})	137.9	41.1	47.7	9.4
Median ammonium (mg L^{-1})	0.1	0.1	0.2	0.2
Median ammonium (kg d^{-1})	4.6	2.0	6.4	1.3
Median SSC (mg L^{-1})	434.4	411.4	293.1	311.8
Median SSC (kg d^{-1})	23,120.5	7625.6	10,856.3	1446.5

Table 4 Spearman correlation coefficient between variables at both watersheds. Grey filled cells indicate statistically significant relationship between the variables ($P < 0.05$). SRP represent soluble reactive phosphorus and TP represent total phosphorus.

Watershed	Variable	Discharge ($\text{m}^3 \text{s}^{-1}$)	Turbidity (NTU)	NO_3^{-1} (mg L^{-1})	NH_4^{+1} (mg L^{-1})	SRP (mg L^{-1})	TP (mg L^{-1})
LRDB	Rainfall (mm)	0.30	0.36	0.14	0.28	-0.08	0.30
	Discharge ($\text{m}^3 \text{s}^{-1}$)		0.69	0.36	0.55	-0.40	0.23
	Turbidity (NTU)			0.11	0.35	-0.21	0.27
	NO_3^{-1} (mg L^{-1})				0.38	-0.13	0.03
	NH_4^{+1} (mg L^{-1})					-0.20	-0.03
	SRP (mg L^{-1})						0.22
LSFB	Rainfall (mm)	0.29	0.28	0.07	0.14	-0.13	-0.02
	Discharge ($\text{m}^3 \text{s}^{-1}$)		0.40	0.55	0.36	0.03	0.32
	Turbidity (NTU)			0.20	-0.14	-0.07	0.24
	NO_3^{-1} (mg L^{-1})				0.50	-0.04	0.34
	NH_4^{+1} (mg L^{-1})					0.01	0.04
	SRP (mg L^{-1})						-0.17

Figure Captions

Figure 1 Location of Little River Ditches Basin (LRDB) and Lower St. Francis Basin (LSFB) on the top. Instream monitoring stations (green circles) and edge-of-field (EOF) stations (red triangles) at Lower St. Francis Basin (left) and Little River Ditches Basin (right) on the bottom. W1 and M2 are outlet of watersheds. Water flows from W9 to W1 and M10 to M2 (right to left) as represented by arrows. EOF sites are part of another study and not measured in this investigation.

Figure 2 Daily turbidity (I-II), nitrate (III-IV), ammonium (V-VI), soluble reactive phosphorous (VII-VIII) and total phosphorous concentrations (VII-VIII) at LRDB (left) and at LSFB (right). Us and Ds in the parentheses represent upstream and downstream. The horizontal lines in box plot represent 10, 25, 50, 75, and 90th percentiles. Above each box in a plot, different letters represent statistical significance at 5% confidence level.

Figure 3 Monthly rainfall (I-II), discharge (III-IV) and turbidity (V-VI) at LRDB (left) and LSFB (right). The values are monthly median and the error bars represent interquartile range.

Figure 4 Nitrate-N (I-II) and ammonium-N (III-IV) concentrations at LRDB (left) and LSFB (right). The values are monthly median and the error bars represent interquartile range.

Figure 5 Soluble reactive phosphorous (SRP)(I-II) and total phosphorous (III) concentrations at LRDB (left) and LSFB (right). The values are monthly median and the error bars represent interquartile range.