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WATERSHED INVESTIGATIVE SUPPORT TO THE POTEAU VALLEY IMPROVEMENT AUTHORITY STREAM WATER QUALITY TO SUPPORT HUC 12 PRIORITIZATION IN THE LAKE WISTER WATERSHED, OKLAHOMA

Watershed Investigative Support to the Poteau Valley Improvement Authority

Stream Water Quality to Support HUC 12 Prioritization in the Lake Wister Watershed, Oklahoma

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INTRODUCTION

Nonpoint source pollution associated with human land use (agriculture and urbanization) is one of the leading causes of impairment to waterways in the United States (EPA, 2000). The primary pollutants associated with agricultural and urban land use are sediment and nutrients which enter nearby streams during rain events and are then carried downstream. These sediments and nutrients may result in water quality issues in the downstream water bodies like increased algal growth or decreased water clarity (e.g. Smith *et al.*, 1999).

Nonpoint source pollution can be mitigated through the implementation of best management practices (BMPs). However, the implementtation of these BMPs should be targeted to areas where these practices will have the greatest effect (Sharpley *et al.*, 2000). Most often watershed models such as the Soil and Water Assessment Tool (SWAT) (Arnold *et al.*, 1998) and Hydrologic Simulation Program Fortran (HSPF; (Bicknell *et al.*, 1996) are used to prioritize subwatersheds or the target locations for BMPs. However, oftentimes these models are applied in watersheds where discharge and water quality data are limited or not available (Fernandez *et al.*, 2000; Evans *et al.*, 2003),

especially at the subwatershed scale being used to target BMP implementation.

Alternatively, recent work suggests that water quality monitoring during base flow conditions can be used to prioritize subwatersheds for BMP implementation (McCarty and Haggard, 2016). Stream nutrient concentrations generally increase with the proportion of agricultural and urban land use in the drainage area (Haggard *et al.*, 2003; Cox *et al.*, 2013; Giovannetti *et al.*, 2013). The premise is that stream water quality during base flow conditions is reflective of the influence of nonpoint source pollution across the watershed. Thus, stream water quality can be related to human land use (i.e., percent urban and agriculture land cover) across a target watershed and this relation can be used to suggest subwatershed priorities.

Lake Wister is on Oklahoma's 303(d) list for impaired water quality, including excessive algal biomass, pH, total phosphorus (TP), and turbidity (ODEQ, 2014). To address these water quality issues, the Poteau Valley Improvement Authority (PVIA) released its "Strategic Plan to Improve Water Quality and Enhance the Lake Ecosystem" in 2009. The strategic plan breaks down the restoration efforts into three zones of action to focus on including the watershed, the full lake, and Quarry Island Cove, and this study focused

on the watershed. The purpose of this project was to monitor stream water quality during base flow conditions at or near the outlets of the subwatersheds, in the Oklahoma portion of the Lake Wister Watershed (LWW). The Oklahoma Nonpoint Source Management Program Plan suggests that monitoring and assessment at the HUC 12 subwatershed scale is the most effective means to identify water quality problems associated with nonpoint source pollution (NPS Management Program Plan, 2014). The primary goal of this monitoring was to assist PVIA and other stakeholders in identifying the HUC 12 subwatersheds where implementation of BMPs could be prioritized to address sediment and nutrient transport from the landscape.

STUDY SITE DESCRIPTION

The LWW covers an area of 2,580 km² (~640,000 acres) and makes up the southern half (52%) of the entire Poteau River sub-basin (HUC 11110105; Figure 1). The LWW is divided into 10 digit hydrologic unit code or HUC 10 watersheds, one entirely within Arkansas the headwaters of the Poteau River watershed, two that traverse the state line between Oklahoma and Arkansas the Black Fork Poteau River and the Poteau River watersheds, and two entirely within Oklahoma the Middle Poteau River and Fourche Maline watersheds. The HUC 10 watersheds that make up the LWW range in size from 377 to 675 $km²$ (93,300 to 166,800 acres). The primary land use and land cover (LULC) across the Oklahoma portion of the LWW is 72% forest, 19% agriculture, and 4% urban; the LULC for the 845 $km²$ (~209,000 acres) portion of the LWW in Arkansas is similar with 71% forest, 20% agriculture, and 5% urban.

Within the Oklahoma portion of the LWW there are 26 HUC 12 subwatersheds that range in size from 42 to 125 km^2 (10,300 to 30,800 acres; Table 1). Forest is the dominant LULC across the HUC 12s, ranging from 45 to 95% of the

watershed. The proportion of human development (i.e., agriculture plus urban) was less than half of the LULC across the HUC 12s (4−48%; Table 1). Additionally, across the LWW there are 7 EPA national pollutant discharge elimination system (NPDES) permitted point sources, including waste water treatment plants (WWTPs), sewage systems, and a poultry processing plant (Table 2).

For this study we selected 26 sampling sites near the outflow of 23 of the HUC 12's in the Oklahoma portion of the LWW (Figure 1; Table 3). The LULC for the catchments upstream of the 26 sample sites ranged from 49−95% forest, <1−37% agriculture, and <1−10% urban. While these sampling sites are located near the outflow of many of the HUC 12s within the Oklahoma portion of the LWW, they represent the catchment area upstream of them and not specifically the HUC 12s.

METHODS

Sample Collection and Analysis

Water samples were collected at the 26 sites at approximately monthly intervals during base flow conditions from July 2016 through July 2017 (following the approved quality assurance project plan). Water samples were not collected in November 2016 because several stream reaches were dry. The samples were collected from the vertical centroid of flow where the water is actively moving either by hand or by an Alpha style horizontal sampler lowered from the bridge. Water samples were split, filtered, and acidified in the field based on the specific storage needs for each analyte. Field duplicate water samples were collected at 10% of the sites within each monthly sampling event; these field duplicates were collected in the same fashion as the original water sample. Additionally, a field blank was collected during each sampling event. A summary of field quality assurance and quality control (QA/QC) data can be found in Appendix

1. All samples were stored on ice until delivered to the Arkansas Water Resources Center certified Water Quality Labs (AWRC WQL).

In addition to the routine monthly sampling, water samples were collected within select HUC 12 subwatersheds to further understand the spatial variability in water quality and potential

sources of nutrients within them. Additional sites were sampled within the Poteau River, Bandy Creek, Shawnee Creek, and Coon Creek (Fourche Maline) HUC 12 subwatersheds (Figure

1). The sites were sampled a total of three times over the month of January 2017. All samples were collected and processed in the same manner as routine monthly samples.

Table 1: Hydrologic unit code (HUC) 12 subwatersheds in the Oklahoma portion of the Lake Wister Watershed and corresponding LULC data, organized at the HUC 10 watershed scale.

¹ % Forest, includes deciduous, evergreen and mixed forest; ² % Agriculture, includes crops, grassland, and pasture/hay; ³ % Urban, includes barren, developed-open space, low, medium, and high intensity development; ⁴ % Human Disturbance Index is the sum of % Agriculture and % Urban.

Table 2: National Pollution Discharge Elimination System (NPDES) permitted sites within the Lake Wister Watershed in Arkansas and Oklahoma.

¹ Waste water treatment plant

All water samples, field duplicates, and field blanks were analyzed for anions (Cl and SO₄), ammonia-nitrogen (NH4-N), nitrate-N plus nitrite-N (hereafter, $NO₃-N$), total N (TN), soluble reactive phosphorus (SRP), total P (TP), turbidity, total suspended solids (TSS) and sestonic chlorophyll-*a* (chl-*a*) using standard methods (Table 4). The analytical techniques, reporting limits and method detection limits are provided (Table 4), and additional information about the certified labs are available at: [https://arkansas](https://arkansas-water-center.uark.edu/water-quality-lab.php)water-**center**[.uark.edu/water-quality-lab.php](https://arkansas-water-center.uark.edu/water-quality-lab.php) (date acquired 12/29/2017).

Data Analysis

All LULC data for the LWW, HUC 12s within the LWW, and catchments upstream of each sampling location were compiled using GeodataCrawler http://www.geodatacrawler. com/ (Leasure, 2013) and Model My Watershed <https://app.wikiwatershed.org/> (date acquired 1/31/2018). Within this LULC data forest is defined as the sum of deciduous, evergreen, and mixed forest, agriculture is the sum of pasture/hay, row crop, and grassland, and urban is the sum of barren, developed open, and low, medium, and high intensity development. Previous, studies from northwest Arkansas have found stream nutrient concentrations to increase with increasing percent agriculture and urban area upstream (Haggard *et al.*, 2003; Giovannetti *et al.*, 2013). Because of this, a simple human disturbance index (HDI) was calculated as the total percent agriculture and urban land use for the catchment upstream of each sample site and for each subwatershed (Tables 1 & 3).

All water quality data collected over the course of this study can be found in the data report "DR-WQ-MSC385" https://arkansas-water-center. uark.edu/publications/DR-WQ-MSC385_Waterquality-monitoring-Poteau-Valley-Improvement -Authority.xlsx) (last accessed 02/15/2018). Annual summary statistics (geometric mean, arithmetic mean, standard deviation, and 5th, $25th$, $50th$, $75th$, and $95th$ percentiles) for each parameter organized by site are reported in Appendix 2. The geomean of constituent concentrations at each site was used in the data analysis, because it is less sensitive to extreme low and high values than arithmetic means. The geomean is typically a good estimate of the central tendency or middle of the data.

Both seasonal and annual geomeans were calculated for the water quality parameters at each site. The geomeans of all the data from each site were related to HDI using simple linear

Table 3: Sample sites and land cover within the Lake Wister Watershed organized by HUC 10s. The number in the HUC 12 column is the final two digits associated with the HUC10 number listed at the top of each group of sites.

¹%Forest, includes deciduous, evergreen and mixed forest; ²%Agriculture, includes crops, grassland, and pasture/hay; ³% Urban, includes barren, developed-open space, low, medium, and high intensity development; ⁴ %Human Disturbance Index is the sum of %agriculture and %urban; and * indicates sites downstream of EPA NDPES permitted point sources.

regression. This statistical analysis shows how geomean concentration increases across a gradient of HDI, or agriculture plus urban land use in the drainage area. The predictive equation, associated with the linear regression, may have some merit in setting achievable water quality targets across the LWW. We cannot

expect a stream with relatively high HDI to have constituent concentrations reflective of near background conditions. However, it may be feasible to expect streams with constituent concentrations well above the regression line to be reduced to near or below the line.

Changepoint analysis is another way to examine how HDI might influence constituent concentrations in streams. Changepoint analysis looks for a threshold in the geomean concentration and HDI relation, where the mean and variability in the data changes. This statistical analysis is not dependent on data distributions, and it gives a threshold in HDI where the geomean concentrations likely increase.

RESULTS AND DISCUSSION

Nitrogen

Geomean concentrations of NH3-N across the streams were 0.03-0.17 mg L^{-1} , where 88% were less than the lab's reporting limit (0.05 mg L^{-1}). Ammonia concentrations were generally low across all seasons, but the variability tended to increase in summer and fall (Figure 2E). During these seasons, geomean $NH₃-N$ concentrations exceeded 0.1 mg L⁻¹ at a few streams. Overall, we would not expect to see relatively high NH₃-N concentrations (except maybe downstream from effluent discharges (Merbt *et al.*, 2011) because it is quickly nitrified in streams (Haggard *et al.*, 2005).

Nitrate concentrations were relatively low across the streams sampled, where annual geomean concentrations of $NO₃-N$ varied from 0.01 to 0.22 mg L^{-1} . There were no clear seasonal patterns of $NO₃$ -N across all of the streams, possibly because $NO₃$ -N geomean were less than 0.1 mg L^{-1} at most sites during each season; however, NO₃-N was a little more variable during the winter (Figure 2C) which may be from increased groundwater inputs and reduced denitrification when temperatures are colder (Martin *et al.*, 2004).

The majority of TN in the flowing waters was in the particulate form, where dissolved inorganic N (DIN: NH₃-N plus NO₃-N) was typically less than 35% of the total. Annual geomean concentrations for TN ranged from 0.10 to 1.50 mg L^{-1} . This range in TN is fairly consistent across all four seasons, and there was no real seasonal pattern (Figure 2A). Overall, nitrogen concentrations tended to be within the range nutrient supply threshold concentrations needed to promote algal growth and cause shifts in algal community composition (0.27-1.50 mg L-1 ; (Evans-White *et al.*, 2013), potentially creating nuisance algal conditions.

The geomean concentrations of the N species varied across the LWW, reflecting changes in nutrients sources and land uses within the drainage areas. The geomean N concentrations increase with the proportion of agriculture and urban development (Figures 3A, C, &E), i.e., HDI values, in the watershed, explaining:

- \bullet 36% of the variability in NH₃-N,
- \bullet 33% of the variability in NO₃-N, and
- 78% of the variability in TN.

These relationships with stream N concentrations and HDI have been observed across the region (e.g. see Haggard et al. 2003; Migliaccio & Srivastava 2007; Giovannetti et al. 2013). The regression lines provide a possible water-quality target to where N concentrations might be reduced at a given HDI. The sites, or streams, with concentrations well above this line might be of specific interest for management, e.g. Site 23.

Figure 2: Box and whisker plots of constituents showing medians (horizontal line within each box), range (error bars show the 5th and 95th percentiles), and outliers (points above and below error bars) for each of the constituents analyzed at the Oklahoma sites in the Lake Wister Watershed. Annual data are to the left of the vertical line, while seasonal data are to the right.

The geomean concentrations of the N species also showed changepoints or threshold responses to increasing HDI; that is, the average and deviation of the geomeans increased above an HDI value. The changepoints were relatively

Figure 3: Simple linear regression of geomean constituent concentrations verse human disturbance index (HDI) values for the Oklahoma portion of the Lake Wister Watershed. The site number in red is Shawnee Creek at highway 59 downstream of effluent discharge, thus it was not used in the statistical analysis.

30% HDI (Figures 4A, C, &E). The average of the data above the changepoint was generally 2 to 3 times greater than the data below that HDI

Figure 4: Change point analysis of geomean concentrations verse human development index (HDI) value for sites in the Oklahoma portion of the Lake Wister Watershed. The vertical dashed line represents the change point values specific to each constituent. The gray box shows the 90% confidence interval about the changepoint. Horizontal bars represent the mean of the data points to the left and right of the change point. The site number in red is Shawnee Creek at highway 59 downstream of effluent discharge was not used in the statistical analysis.

be scrutinized further to identify sites that might be of management interest.

Phosphorus

Geomean concentrations of SRP across the streams ranged from 0.005 to 0.041 mg L^{-1} , with 60% of the values measured were less than the lab's reporting limit (0.01 mg L^{-1}). Geomean concentrations of SRP were fairly similar across each of the seasons with the exception of summer, where there is a slight increase across the sites overall (Figure 2D). The slight increase in SRP during the summer might be related to mineralization or released from the stream bottom during warmer conditions (Banaszuk and Wysocka-Czubaszek, 2005) and when groundwater inputs are less. However, overall SRP concentrations across the streams of the LWW were low with majority of sites having geomean concentrations less than 0.01 mg L^{-1} .

Geomean concentrations for TP ranged from 0.013 to 0.208 mg L^{-1} ; much of which was in the particulate form, where the dissolved form (SRP) typically made up less than 33% of the measured TP. This range was fairly consistent across all of the seasons except for summer, where concentrations were slightly elevated (Figure 2B). The increase in TP across the streams during summer corresponded with the slight increase in SRP, as well as slight increases in sediment and Chl-*a* in the water column (discussed later). Like TN, TP concentrations tended to be within the range or nutrient supply threshold concentrations needed to increase algal growth and drive shifts is algal community composition in streams (0.007 – 0.100 mg L-1 ; (Evans-White *et al.*, 2013) and potentially cause nuisance algal conditions; although, two sites with values much higher than this range were directly downstream of effluent discharges (Bandy Creek and Shawnee Creek at Hwy 59).

Geomean P concentrations varied across the streams draining the LWW, showing that over

65% of the variability in P concentrations was explained by HDI (Figures 3B & C). These relationships between stream P concentrations and HDI, like N species, have been observed across the region (e.g. see (Haggard *et al.*, 2003; Cox *et al.*, 2013), reflecting the potential P sources such as poultry litter applied to pastures (DeLaune *et al.*, 2004; Cox *et al.*, 2013). The regression lines provide a realistic water quality target to where P concentrations might be reduced and show sites that deviate greatly from concentrations at a given HDI.

The geomean concentrations of the P species also showed changepoint responses to increaseing HDI. The changepoints for P species were slightly more variable than for N species, ranging from 21 to 30% HDI. In both cases mean values to the right (above) of the threshold were more than 2 times greater than the mean values to the left (below) of the threshold. Site 23 consistently shows elevated P and N concentrations relative to other sites across the LWW, suggesting nutrient sources upstream might need to be investigated (Figure 4B & C).

Suspended Sediments and Turbidity

Annual geomeans for turbidity and TSS were from 6 to 57 NTU and from 1 to 31 mg L^{-1} , respectively. These two constituents were strongly correlated (r=0.97; P<0.001) and show similar seasonal patterns, with greater values in the spring and summer and lesser values in the fall and winter (Figures 2F & H). Low values in the fall, for both constituents, may be explained by the drier conditions that began towards the end summer through early winter 2016. The less frequent rainfall events producing runoff reduces erosion from the landscape and within the fluvial channel, and the lower flows throughout this season have less power to erode the channel and keep particulates in the water column (Morisawa, 1968). The more frequent storms and elevated base flow during spring and

early summer likely keep TSS and turbidity elevated in streams (relative to fall) across the LWW. Turbidity and TSS often are positively correlated to TP in streams (Stubblefield *et al.*, 2007), which was also the case across the streams in the LWW (r=0.739; P<0.001).

Many factors influence turbidity and the amount of particulates in the water column of streams, including rainfall-runoff, discharge, channel erodibility, and even algal growth to some degree. The myriad of factors that influence turbidity (and particulates) in water are also influenced by human activities, which is likely why HDI explained more than half of the variability in geomeans of turbidity and TSS across the streams of the LWW (Figure 3F & H). These relations are not well defined regionally but where data is available similar observations have been made (Price and Leigh, 2006). While these regressions were significant, there was also a significant threshold response in turbidity and TSS at 22-28% HDI (Figure 4F & H). It is interesting that turbidity and TSS, during base flow conditions were so strongly correlated to HDI across these sites.

Chlorophyll a

Annual geomean concentrations of sestonic Chl*a* (algal biomass in the water column) ranged from 0.5 to 12.6 μ g L⁻¹ across the streams in the LWW. Geomean Chl-*a* concentrations were consistent throughout the year, without much variability between seasons (Figure 2G). Geomean Chl-*a* concentrations across these sites were strongly (positively) related to total nutrient concentrations in the water column where TP explained 78% on Chl-*a* variability (P<0.001), while TN explained 85% (P<0.001). The sites with elevated Chl-*a* had increased total nutrient concentrations and supply available, as has been the case in other systems (Chambers *et al.*, 2012; Haggard *et al.*, 2013)

The geomean concentrations of Chl-*a* increased with the proportion of human development in the watershed (i.e., HDI values), where HDI explained 59% of the variability in sestonic Chl-*a* (P<0.001; Figure 3G). This strong relationship was surprising, because many physical, chemical, and biological factors influence algal growth in streams (Evans-White *et al.*, 2013). However, in steams hydrology (e.g. discharge; Honti et al. 2010) is one of the most important factors since most algal growth would be on substrates not generally in the water column (i.e., sestonic). It is likely that this correlation is driven by the increased nutrient concentrations that would be found at sites with higher HDI values. Interestingly, sestonic Chl-*a* still showed a threshold at an HDI value (28%) similar to that observed with the chemical concentrations (Figure 4G).

Anions

Annual geomean concentrations of Cl ranged from 2 to 17 mg L^{-1} . Geomeans for CI increased during the winter, this was likely due to greater groundwater inputs during the winter (Figures 2I & J). Also, greater Cl concentrations of both anions may have been caused by use of road deicers used during icy road condition as has been found elsewhere (Sun *et al.*, 2014). Despite having greater concentrations in the winter, Cl was consistently below EPA secondary drinking water standards of 250 mg L^{-1} across all sites sampled. Relatively few studies have focused on toxicity of Cl on freshwater fish. However, the reported values in this study for Cl were 2 to 3 orders of magnitude less than those reported to have chronic toxicity effects on fat head minnows and rainbow trout [704 mg L^{-1} and 1174 mg L-1 , respectively (Elphick *et al.*, 2011b)].

Annual geomean concentrations of $SO₄$ ranged from 2 to 39 mg L⁻¹. Like Cl, Geomeans for SO₄ increased during the winter, this was likely due to greater groundwater inputs during the winter (Figures 2J), or possibly from the use of road deicers used in the winter (Sun *et al.*, 2014). Sulfate concentrations were consistently below EPA secondary drinking water standards of 250 mg L^{-1} across all sites sampled. Chronic toxicity of SO⁴ on aquatic organisms varies in relation to the water hardness, with greater SO₄ toxicity under soft water conditions (hardness<80 mg L^{-1} measured as $CaCO₃$) which is common in sandstone dominated systems such as the LWW. Sulfate values measured were lower than suggested standards for protecting aquatic life in soft water systems [129 mg L⁻¹ SO₄ (Elphick *et al.*, 2011a)].

The geomean concentrations of both Cl and SO₄ were both positively related to the HDI gradient within the Oklahoma portion of the LWW, explaining 32% of the variability for Cl and 49% of the variability for SO_4 (Figure 3I & J). The geomean concentrations of these two anions also showed changepoint responses to increaseing HDI, which were similar between constituents (15−18% HDI) but slightly less than other parameters. The average value for the data above the changepoint tended to be 2 to 3 times greater than the average of the values below the changepoint line (Figure 4I & J).

Comparing Oklahoma and Arkansas streams

We compared annual geomean concentrations from this study (i.e. the Oklahoma side of LWW) to geomeans measured in a previous study from the Arkansas portion of the Poteau River Subbasin (Massey *et al.*, 2013) to understand how concentrations might vary across state lines and along the HDI gradient. The Arkansas data used in this comparison was collected from December 2011 through October of 2012, five years earlier than this study period. We recognize that this discrepancy in time frames may impart some temporal variability due to differences in hydrology and potential land use changes that may have occurred. However, the merging of these together expanded our gradient of HDI.

The HDI across Arkansas streams was almost twice as high (1-90%) as the range for streams in the Oklahoma portion of the LWW (4-48%).

Overall, the data from this study and the Arkansas study (Massey *et al.*, 2013) fit well together across the HDI gradient. The comparisons can be summarized by (Figure 5):

- annual geomean concentrations for $NO₃$ -N were greater across Arkansas streams than Oklahoma streams;
- annual geomean concentrations for TN were slightly greater in Arkansas streams than Oklahoma streams;
- annual geomean concentrations for TP were slightly greater in Arkansas streams than Oklahoma streams;
- annual geomean concentrations for SRP were less in Arkansas streams that Oklahoma streams;
- annual geomeans for turbidity and TSS were relatively similar between studies.

The increased $NO₃$, TN, and TP concentrations for the Arkansas streams (relative to this study) is likely due to the sampling of streams with a greater range of human development in the watershed. Again, these data generally fit well together (overlapped each other) across the HDI gradient.

The exception was SRP, which showed divergence between the data across the HDI gradient (Figure 5D). While SRP generally increased with HDI in both Arkansas and Oklahoma streams, the increase (or slope) was much greater per unit increase in HDI with the Oklahoma data verse Arkansas. The difference in SRP availability in the water column is interesting, and future studies might try to ascertain why.

Special Studies

A few of the subwatersheds or sampling sites, were of specific interest to PVIA, including Bandy

Figure 5: Scatter plot of annual geomean concentrations versus human disturbance index (HDI) for sites sampled in this study (black circles) and for sites in the Arkansas portion of the Poteau River Watershed (gray circles) sampled during the 2011-2012 sample year (Massey *et al.*, 2013). The box plots showing the distribution of geomean concentrations for streams in Arkansas and Oklahoma are depicted in the upper right hand corner of each panel.

Creek (site 23), Fourche Maline (site 24), Poteau River (sites 1-3), and Shawnee Creek (site 26). We sampled additional sites within these subwatersheds to help PVIA understand where potential nutrient and sediment sources might be or to confirm the influence of a known specific source. The additional sampling was short-term (n=3, January 2017), but provided the information needed.

The primary objective the Poteau River subwatershed was to determine whether the nutrient and sediment source was flowing in from upstream or if the tributaries flowing in were also possible issues. We sampled four

inflowing tributaries and the three sites along the Poteau River (Figure 1). These additional data showed:

- Three tributaries (P1, P2, and P3) had nutrient and sediment concentrations reflective of or less than expected based on watershed land use.
- One tributary (P2) had elevated SO⁴ concentrations (271 mg L^{-1}) relative to the other sites (except P4).
- One tributary (P4) had elevated constituent concentrations (except sediment and turbidity) and should be further evaluated (Figure 6).

Figure 6: Geomean concentrations across the sites along the Poteau River sampled in January 2017 for the special study. With geomean concentrations of TN **(A)**; TP **(B)**; and TSS **(C).**

Overall, the tributaries (except P4) have nutrient and sediment concentrations reflective of the watershed land use (i.e., HDI value). However, one tributary (P4) has high concentrations all likely driven by the effluent discharge at Heavener, Oklahoma. The effects of this tributary and effluent discharge were not

observed in the Poteau River, because a (much) larger tributary (Black Fork) with a low HDI flows in and has low constituent concentrations.

For the Fourche Maline subwatershed we wanted to see how far upstream into the headwaters were higher constituent concentrations found. So, we sampled five additional sites upstream plus the main site on the Fourche Maline (Figure 1). These additional data showed:

- All five sites in the headwaters of the Fourche Maline had constituent concentrations reflective of the watershed land use, with a few exceptions.
- One site (F5) had elevated sestonic Chl-*a* concentrations (19.2 µg L-1 Chl-*a*).
- Two sites (F1 and F5) had elevated Cl concentrations (50 and 150 mg L^{-1} , respectively) much greater than expected based upon the upstream land use.
- Two sites (F4 and F5) had elevated nutrient and sediment concentrations, greater than expected based upon upstream land use (Figure 7).

These findings suggest that, for the most part, the headwaters of the Fourche Maline have relatively low constituent concentrations that are reflective of the changes in land use as you move upstream. It is possible that road salts resulted in elevated Cl concentrations (especially at F5), since samples were collected during winter when deicing agents are added to the roadway.

Bandy Creek has an NPDES permitted facility (Table 2) and effluent discharge upstream from our routine sampling site (23), so the goal of this special study was to see if the effluent discharge was the sole source. We selected five sites along Bandy Creek and a select tributary, including four sites upstream from the effluent discharge (Figure 1). These data showed:

 All four sites upstream of the effluent discharge had constituent concentrations

Figure 7: Geomean concentrations across the sites along the Fourche Maline sampled in January 2017 for the special study. With geomean concentrations of TN **(A)**; TP **(B)**; and TSS **(C).**

reflective of the watershed land use or slightly less.

 The site downstream from the effluent discharge (B4) had elevated concentrations for all N species, including the greatest TN and $NO₃$ concentrations measured during that period.

 One site upstream of the effluent discharge (B1) had elevated nutrient and sediment concentrations, greater than the other three upstream sites (Figure 8).

These findings suggest that the primary factor influencing the water quality in this particular watershed is the WWTP in Wilburton, Oklahoma. However, what was surprising is that the two sites (B1 and B2) with the highest proportion of human development across all of the Oklahoma sites (~77% HDI) had relatively low constituent concentrations.

While Shawnee Creek (sites 13 and 26) drains a forest watershed (~93%), the PVIA had concerns about the effluent discharge at the Jim E. Hamilton Correctional Center. The goal here was to evaluate constituent concentrations upstream and downstream of this effluent discharge, so we sampled three sites upstream, one site directly below the discharge and then our two routine sites further downstream (Figure 1). The primary findings from this study include:

- With the exception of turbidity, all constituent concentrations for the sites upstream of the effluent discharge were reflective of that expected from a forested watershed.
- Turbidity was elevated at all sites, except for the most downstream site (13).
- The effluent discharge significantly increasees nutrient, sediment, and sestonic Chl-a concentrations at Shawnee Creek (Figure 9).

These data show that effluent discharge at Shawnee Creek influences water quality. However, this effect seems to be localized or just relatively close proximity to the effluent source. The furthest downstream site (13) on Shawnee Creek has low constituent concentrations. For example TP concentrations were 0.247 mg $L^{\text{-}1}$ at Hwy 59 (site 26) and were only 0.013 mg L^{-1} at site 13 just over 3 km (2 miles) downstream. The

Figure 8: Geomean concentrations across the sites along Bandy Creek sampled in January 2017 for the special study. With geomean concentrations of TN **(A)**; TP **(B)**; and TSS **(C).** The vertical dashed line represents the NPDES permitted discharge into Bandy Creek.

forested watershed plays a role in diluting and retaining the nutrients in Shawnee Creek.

Overall, with the exception of sites largely influenced by effluent discharges, the sites for the smaller catchments had constituent concentrations that rather closely aligned with the routine monitoring sites. The data when merged

together followed the patterns shown earlier with only the routine sites. This suggests that these constituent concentrations respond to watershed land use in streams small to relatively large watersheds. These statistics (e.g., regression models and changepoints) are likely useful over a wide range of watershed sizes.

Criteria for Selecting Priority HUC 12s.

Changepoint analysis is a powerful statistical tool, and one of its most useful aspects is that it gives a threshold, i.e., specific value on the x−axis. In this case, the changepoint gives an HDI value or the proportion of the watershed that is agriculture and urban. This is the point where watershed land use has an influence on water quality, increasing the constituent concentrations. Thus, this information can be used to help design a process from which PVIA and its stakeholders could establish which HUC 12s or smaller subwatersheds were priorities for NPS management. The following sections provide some guidance on how this might be done.

In the absence of water quality data at all subwatersheds, specific HDI thresholds can be used to help identify which HUC 12s or smaller watersheds might be a priority for NPS management. The HUC 12s could be prioritized and separated into categories based on the example (Figure 10A). The hypothetical categories could include:

- Preservation: HDI<15%; these subwatersheds would be background or reference sites as established by the lower end of the 90th percentile confidence interval about the changepoints.
- Low priority: HDI from 15-25%; these subwatersheds would be a low priority for NPS management as established by the lower end of the 90th percentile confidence interval about the changepoint and the changepoints.

Figure 9: Geomean concentrations across the sites along Shawnee Creek sampled in January 2017 for the special study. With geomean concentrations of TN **(A)**; TP **(B)**; and TSS **(C).** The vertical dashed line represents the NPDES permitted discharge into Shawnee Creek.

 Medium priority: HDI from 25-30%; these subwatersheds would be a medium priority for NPS management as established by the changepoint and the upper end of the 90th percentile confidence interval about the changepoints.

 High priority: HDI>30%; these subwatersheds would be a high priority for NPS management as established by the upper end of the 90th percentile confidence interval about the changepoints

Based on the LWW stream data, sites with HDI values less than 90th percentile confidence interval about the changepoint had low constituent concentrations (Figure 10A). The goal here would be to keep or preserve these HUC 12s to maintain existing water quality conditions. On the opposite end of the spectrum, streams with HDI values greater than the 90th percentile confidence interval around the change point generally had greater constituent concentrations. So, PVIA and stakeholders might want to focus efforts on HUC 12s with HDI values above 30% when establishing NPS management priorities. If we just use the LULC for each individual HUC 12 (Table 1), then following this classification scheme the priority areas would be the Fourche Maline and one HUC 12 along the Poteau River in Oklahoma (Figure 11). In the absence of water quality data, this option can be a good method for selecting HUC 12s when developing the watershed management plan.

When water quality data is available, thresholds can be used differently to select HUC 12s based on measured constituent concentrations as opposed to predicted values that are based on human development (Figure 10B). This method focuses on the average constituent concentrations on either side of the threshold. The HUC 12s could be prioritized and separated into categories based on the example in Figure 10B. The hypothetical categories could include:

 Low priority: HUC 12s with constituent concentrations less than average constituent concentration below the threshold

Figure 10: Potential methods using changepoints to identify watersheds for nonpoint source management. Categorization of HUC 12s based on their human disturbance index (HDI) value only **(A)**; separation of HUC 12s based on measured water quality data **(B).** Linear models (regression line) represent realistic targets for improving water quality within a HUC 12 of a given HDI value **(C)**.

plus 2 standard deviations (horizontal dashed line; Figure 10B).

 Medium priority: HUC 12s with constituent concentrations greater than the horizontal dashed line but less than the

average constituent concentration above the threshold (upper solid line; Figure 10B)

 High Priority: HUC 12s with constituent concentrations greater than upper solid line.

As stated earlier, constituent concentrations below the thresholds were generally low. The horizontal dashed line provides a realistic bench mark for separating low and medium priority watersheds, as it represents the upper limits of baseline conditions for the constituents analyzed in this study. This method could be carried out for each constituent of interest, resulting in the selection of constituent specific HUC 12s (Figure 12).

A weight of evidence approach may be used to combine HUC 12 priorities developed for individual constituents. Low, medium, and high priorities can be ranked 1, 2, and 3, respectively, for each constituent. Rankings for each constit-uent can then be added together to form a cumulative rank for each HUC 12. The cumulative ranks across all HUC 12s within the Oklahoma portion of the LWW were divided into 5 categories where the subwatersheds labeled as the highest priority had the highest rank (Figure 12).

With this approach you must be mindful of the nested nature of the LWW in that several subwatersheds are down river of one or more other

subwatersheds. It is possible that water quality in an upstream subwatershed may result in higher than expected constituent concentrations that expected based on the level of human development. In this case, it may be

Figure 12: Potential prioritization of HUC 12 subwatersheds when chemical concentrations are available in streams. Using specific constituents to meet specific management needs, or using a cumulative approach, where priorities are added across multiple constituents. For each constituent shown and for the cumulative map the priority for nonpoint source management varies from lightest (low priority) to darkest (highest priority). Each subwatershed is labeled with the last four digits of their HUC 12 code.

beneficial to compare subwatershed priorities identified by both methods.

Constituent concentrations change with land use, where the relation can often be described with a simple linear model (Figure 3). Once subwatersheds have been prioritized, the goal should be to move the higher priority HUC 12s below the linear regression which represents the

average conditions at a given HDI level. The methods should follow previous routine monitoring methods used to develop these relationships, where 12 monthly base flow samples should be used to determine an annual geomean concentration data point. The data point should be plotted against the most current land use information available, to reflect the changing LULC and HDI gradient. Once the data

point shifts from above the line to below the line, then this site has reached its target concentration as defined by the original regression. However, it would be wise to make sure the HUC 12s have consistently changed priority categories (e.g., moved from high to low) over multiple years before assuming the end point has been met.

REFERENCES

- Arnold JG, Srinivasan R, Muttiah RS, Williams JR, 1998. LARGE AREA HYDROLOGIC MODELING AND ASSESSMENT PART I: MODEL DEVELOPMENT1. JAWRA J. Am. Water Resour. Assoc. 34:73–89.
- Banaszuk P, Wysocka-Czubaszek A, 2005. Phosphorus dynamics and fluxes in a lowland river: The Narew Anastomosing River System, NE Poland. Ecol. Eng. 25:429– 441.
- Bicknell BR, Imhoff JC, Kittle Jr JL, Donigian Jr AS, Johanson RC, 1996. Hydrological simulation program-FORTRAN. user's manual for release 11. US EPA.
- Chambers PA, McGoldrick DJ, Brua RB, Vis C, Culp JM, Benoy GA, 2012. Development of Environmental Thresholds for Nitrogen and Phosphorus in Streams. J. Environ. Qual. 41:7–20.
- Cox TJ, Engel BA, Olsen RL, Fisher JB, Santini AD, Bennett BJ, 2013. Relationships between stream phosphorus concentrations and drainage basin characteristics in a watershed with poultry farming. Nutr. Cycl. Agroecosystems 95:353–364.
- DeLaune PB, Moore PA, Carman DK, Sharpley AN, Haggard BE, Daniel TC, 2004. Development of a Phosphorus Index for Pastures Fertilized with Poultry Litter— Factors Affecting Phosphorus Runoff Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee by the USDA and does not imply its approv. J. Environ. Qual.

33:2183–2191.

- Elphick JR, Davies M, Gilron G, Canaria EC, Lo B, Bailey HC, 2011a. An aquatic toxicological evaluation of sulfate: The case for considering hardness as a modifying factor in setting water quality guidelines. Environ. Toxicol. Chem. 30:247–253.
- Elphick JRF, Bergh KD, Bailey HC, 2011b. Chronic toxicity of chloride to freshwater species: Effects of hardness and implications for water quality guidelines. Environ. Toxicol. Chem. 30:239–246.
- EPA U, 2000. Atlas of America's Polluted Waters. EPA 840-B00-002. Washington D.C.:
- Evans-White MA, Haggard BE, Scott JT, 2013. A Review of Stream Nutrient Criteria Development in the United States. J. Environ. Qual. 42:1002–1014.
- Evans BM, Lehning DW, Corradini KJ, Petersen GW, Nizeyimana E, Hamlett JM, Robillard PD, Day RL, 2003. J . of Spatial Hydrology. J. Spat. Hydrol. 2:18.
- Fernandez W, Vogel RM, Sankarasubramanian A, 2000. Regional calibration of a watershed model. Hydrol. Sci. J. 45:689–707.
- Giovannetti J, Massey LB, Haggard BE, Morgan RA, 2013. Land use effects on stream nutrients at Beaver Lake Watershed. J. Am. Water Work. Assoc. 105:.
- Haggard BE, Moore Jr PA, Chaubey I, Stanley EH, 2003. Nitrogen and phosphorus concentrations and export from an Ozark Plateau catchment in the United States. Biosyst. Eng. 86:75–85.
- Haggard BE, Scott JT, Longing SD, 2013. Sestonic chlorophyll-a shows hierarchical structure and thresholds with nutrients across the Red River Basin, USA. J. Environ. Qual. 42:437– 445.
- Haggard BE, Stanley EH, Storm DE, 2005. Nutrient retention in a point-sourceenriched stream. J. North Am. Benthol. Soc. 24:29–47.
- Honti M, Istvánovics V, Kovács ÁS, 2010. Balancing between retention and flushing in

river networks—optimizing nutrient management to improve trophic state. Sci. Total Environ. 408:4712–4721.

- Leasure DR, 2013. http://www.geodatacrawler. com. Accessed.
- Martin C, Aquilina L, Gascuel‐Odoux C, Molenat J, Faucheux M, Ruiz L, 2004. Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments. Hydrol. Process. 18:1237–1254.
- Massey LB, Mccarty JA, Matlock MD, Sharpley AN, Haggard BE, 2013.
- McCarty JA, Haggard BE, 2016. Can We Manage Nonpoint-Source Pollution Using Nutrient Concentrations during Seasonal Baseflow? AEL 1:0.
- Merbt SN, Auguet J-C, Casamayor EO, Marti E, 2011. Biofilm recovery in a wastewater treatment plant-influenced stream and spatial segregation of ammonia-oxidizing microbial populations. Limnol. Oceanogr. 56:1054–1064.
- Migliaccio KW, Srivastava P, 2007. Hydrologic components of watershed-scale models. Trans. ASABE 50:1695–1703.
- Morisawa M, 1968. Streams: Their Dynamics and

Morphology. McGraw-Hill Company, New York, NY.:

- Price K, Leigh DS, 2006. Comparative Water Quality of Lightly- and Moderately-Impacted Streams in the Southern Blue Ridge Mountains, USA. Environ. Monit. Assess. 120:269–300.
- Sharpley A, Foy B, Withers P, 2000. Practical and Innovative Measures for the Control of Agricultural Phosphorus Losses to Water: An Overview. J. Environ. Qual. 29:1–9.
- Smith VH, Tilman GD, Nekola JC, 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ. Pollut. 100:179–196.
- Stubblefield AP, Reuter JE, Dahlgren RA, Goldman CR, 2007. Use of turbidometry to characterize suspended sediment and phosphorus fluxes in the Lake Tahoe basin, California, USA. Hydrol. Process. 21:281– 291.
- Sun H, Alexander J, Gove B, Pezzi E, Chakowski N, Husch J, 2014. Mineralogical and anthropogenic controls of stream water chemistry in salted watersheds. Appl. Geochemistry 48:141–154.

APPENDIX 1: QA/QC report

Appendix 1: QA/QC summary for each constituent, including field blanks and field duplicates.

*****Constituents with field duplicates that did not pass the defined criteria in the QAPP. All samples with a high %RPD (>30%) for both $NO₃-N$ and TSS had measured values below the MDL, which can make it difficult to attain a %RPD<30.

APPENDIX 2: Summary Statistics

Appendix 2A: Summary statistics for TN showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2B: Summary statistics for TP showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2C: Summary statistics for NO₃-N showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2D: Summary statistics for NH3-N showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2E: Summary statistics for SRP showing annual geometric means, arithmetic means, standard deviation, and precentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2F: Summary statistics for turbidity showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2G: Summary statistics for TSS showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2H: Summary statistics for Chl-*a* showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in μ g L⁻¹.

Appendix 2I: Summary statistics for Cl showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

Appendix 2J: Summary statistics for SO⁴ showing annual geometric means, arithmetic means, standard deviation, and percentile distributions of the monthly data collected at each of the sites within the Lake Wister Watershed. All values reported are in mg L^{-1} .

