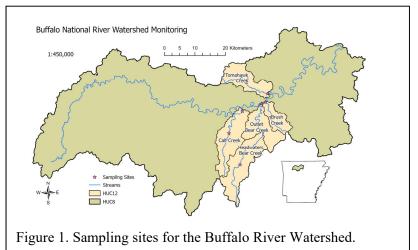
## 19-300 Buffalo River Watershed Monitoring Project Final Report Submitted by Jennifer L. Bouldin Ecotoxicology Research Facility Arkansas State University

# 1. Executive Summary

The objective of this project was to monitor water quality data in the Buffalo River. The Buffalo River (HUC #11010005) was named as the first National River in the US and is designated an Extraordinary Resource Waterway by the ADEQ (2008). The River is listed on the 303d list of impaired waterways for Total Dissolved Solids, Dissolved Oxygen, and temperature (ADEQ, 2018). The major source of the contamination is listed as either agriculture (pasture) or municipal discharge. Soil disturbances from pasture land contribute to the impairment.

Sampling sites were established by Arkansas Natural Resource Division and ASU ERF personnel for four subwatersheds within the Buffalo River Watershed. Headwater and outlet sites were located within each subwatershed to enable measurement of changes in water quality within the subwatershed (Figure 1). Headwater and outlet sampling sites included Tomahawk Creek, Calf Creek, Bear Creek and Brush Creek (Table 1).



Subwatershed	Acronym	HUC#	% Pasture	% Forest
Tomahawk Creek Headwater	TOHD	110100050407	28%	64%
Tomahawk Creek Outlet	TOOT			
Calf Creek Headwater	CAHD	110100050401	27%	64%
Calf Creek Outlet	CAOT			
Bear Creek Headwater	BEHD	110100050404	23%	72%
Bear Creek Outlet	BEOT	110100050403	41%	50%
Brush Creek Headwater	BRHD	110100050405	25%	62%
Brush Creek Outlet	BROT			

Table 1. Sampling sites, acronym, HUC #, % pasture and % forest for each sampled subwatershed in the Buffalo River Watershed. Data from www.modelmywatershed.org.

The A-State Ecotoxicology Research Facility (ERF) began measuring weekly water quality parameters on November 8, 2019, and completed three years of water quality sampling on January 16, 2023. There was a five-week period when no sampling occurred during the closure of National Parks due to COVID. These analytes included total suspended solids (TSS), turbidity, dissolved oxygen, pH, conductivity, dissolved nitrates, nitrites, orthophosphates, and total nitrogen (N) and phosphorus (P).

The greatest TSS and turbidity values were measured in the headwaters of Calf Creek (CAHD) and Brush Creek (BRHD). In both subwatersheds attenuation within the stream resulted in lower TSS and turbidity in the stream outlets (CAOT and BROT). This decrease was most notable in the Brush Creek Subwatershed. BROT TSS and turbidity values were comparable to those measured in Tomahawk Creek (BRHD and BROT), as this subwatershed had the lowest measured values and no substantial change from upstream to downstream were measured.

A single sampling event immediately following a storm event on 04/29/2021 significantly increased the mean TSS and turbidity values. Calculation of means omitting this single event reduced the turbidity values up to 29% and the TSS values up to 49%, illustrating the effect a single storm event can have in these subwatersheds.

Mean values for NO<sub>3</sub> and Total N were substantially greatest in Brush Creek. BROT mean values were greater than BRHD indicating either a dilution effect or attenuation of the nitrogen in this stream. Interestingly, Brush Creek subwatershed has the least amount of pasture (25%) of any of the subwatersheds sampled in this study. However, it has the least stream length of any of the subwatersheds sampled and the greatest terrain slope of any of the sampled subwatersheds (19.2%; www.modelmywatershed.org).

The only subwatershed to increase in mean NO<sub>3</sub> and Total N from headwater to outlet sampling sites was Bear Creek. Three-year mean NO<sub>3</sub> and Total N values had similar increases and approximately doubled from headwater to outlet. Total stream length for Bear Creek is 223km, which is substantially longer than other measured headwater and outlet sites.

This present project was funded at \$688,220 with 44% match from A-State (\$301,898) and federal funds from the ANRD (\$386,322).

# 2. Project Chronology

Following confirmation of sampling sites, weekly collections began on October 2, 2019. Samples were collected from each site using a bucket rinsed in the respective site water, followed by filling the acid-washed sample bottles (1-L Nalgene bottles) as recommended by the ERF Standard Operating Procedure (SOP) and based on American Public Health Association methods (APHA, 2005). Filtered samples for nutrient analyses were accomplished on-site with a syringe and 0.45 µm filter filling two 15-mL centrifuge tubes and unfiltered samples were collected in a 50-mL conical tube for Total N and P. All samples were immediately labeled with site name, collection date and time, and initials of person(s) collecting sample; samples were then placed immediately on ice. Upon returning to the ERF, samples were warmed to room temperature and tested for TSS and turbidity while filtered samples for dissolved nutrients and unfiltered 50-mL subsamples for total N and P were frozen until analyzed. TSS was measured in triplicate using the filtration technique and 100-mL of sample and nutrients were measured using the Skalar SANS++ nutrient analyzer. All water quality tests followed the American Public Health Association (APHA 2005) guidelines.

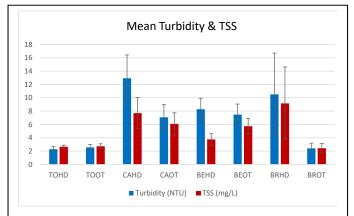
Quality control and quality assurance was accomplished in this project as outlined in the QAPP and the ERF SOP. The ERF is EPA certified (AR#00917) for TSS and nutrients (nitrate, nitrite, orthophosphates) and certification requires bi-annual unknowns by the Arkansas Department of Environmental Quality (ADEQ). Annual re-certification requires reporting acceptable results on EPA unknowns for these parameters.

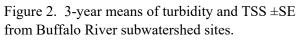
## 3. Results & Discussion

The three-year means of TSS and turbidity were greatest at the headwaters of Calf Creek (CAHD) and Brush Creek (BRHD; Figure 2). Both streams had lower TSS and turbidity measured at each outlet,

however Brush Creek outlet (BROT) had the greatest reduction of any of the measured streams, reducing turbidity and TSS values 77 and 73%, respectively, of the BRHD values. This significant reduction is notable as it includes one substantial rainfall event on 04/29/2023. Omitting the values measured on that day reduces BRHD mean turbidity values from 10.5 to 4.3NTU and mean TSS values from 9.2 to 3.7mg/L (Figure 3). Omission of this sampling date reduces the mean values for all sampled sites. Also notable is Calf Creek; CAHD had the greatest mean turbidity value (12.9NTU) and following the omission of the measured value of 395NTU (see appendices), the mean value was reduced to 10.2NTU. Although other spikes in TSS and turbidity were measured during the sampling period and can be seen in Appendix 1, this single event resulted in an overall increase in all the three-year means, thus Figure 3 is included to illustrate the differences in the three-year means without that single sampling event. The same scale was used in each graph for ease of comparison.

Tomahawk Creek subwatershed TSS and turbidity values did not change significantly from headwater to outlet and mean values were similar to BROT. Bear Creek Outlet subwatershed has the greatest % pasture and least % forested landuse and also had a





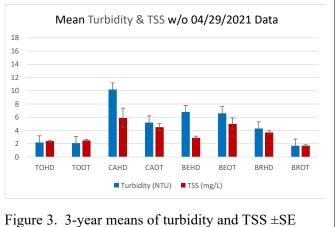


figure 3. 5-year means of turbidity and  $155 \pm 5E$ from Buffalo River subwatershed sites without data from 04/29/2021.

greater mean TSS value at the outlet (BEOT) than the headwater (BEHD), possibly due to the increased percent pasture in Bear Creek Outlet (BEOT) subwatershed as compared to the headwater subwatershed (BEHD) (Table 1). Turbidity values were similar from upstream to downstream for Bear Creek.

With the exception of the TSS mean value for BEOT, upstream to downstream TSS and turbidity values decreased from headwater to outlet in all sampled subwatersheds. This could be a result of sediment attenuation within the stream through channel roughness, sedimentation in pools where water velocity is decreased, or a dilution factor from additional flow from springs in the karst geology of this area.

Brush Creek headwaters and outlet sites (BRHD; BROT) had significantly greater NO<sub>3</sub> and Total N values than other sampled sites (Figures 4,5). Also notable is a reduction in nitrogen values from upstream to downstream. Brush Creek subwatershed has the least amount of pasture (25%) of any of the subwatersheds sampled in this study (Table 1). However, it has the shortest stream length of any of the subwatersheds sampled and the greatest terrain slope of any of these subwatersheds (19.2%; www.modelmywatershed.org), thus biological uptake within the stream and dilution from tributaries will

have less of an affect in this stream than the other sampled subwatersheds due to higher overland flow. The source of high nitrogen values in Brush Creek, especially at BRHD, could not be determined in this study. All subwatersheds had lower mean NO<sub>3</sub> and Total N values at the outlet than the headwater with

the exception of Bear Creek.  $NO_3$  and Total N values increased from BEHD to BEOT, approximately doubling from headwater to outlet. Total stream length for Bear Creek is 223km and actually covers two subwatersheds with increased pasture landuse in BEOT. Stream length in this Buffalo River tributary is also substantially longer than other measured subwatersheds.

Bear Creek subwatershed also had an increase in TSS from upstream to downstream which was not reflected in the PO<sub>4</sub> or Total P values. Phosphorus values often mimic suspended sediment values as they are easily adsorbed onto sediment particles and transported with suspended sediment. In this stream, mean phosphorus values were more similar to mean turbidity values. In addition to being the longest stream in this study, Bear Creek Outlet also supports the greatest amount of pasture (41%) and the least forested landuse (50%) and BEHD landuse includes the least pasture (23%) and most forested (72%). Pasture land in BEOT sampling site most likely contributed to the increased nitrogen values. Cattle pasture land has been cited as resulting in increased nitrogen values in surface waters (Singh et al., 2019), thus landuse most likely was a factor in these increased nitrogen values.

Nitrogen pollution has been cited as a stressor in aquatic systems, is related to species decline

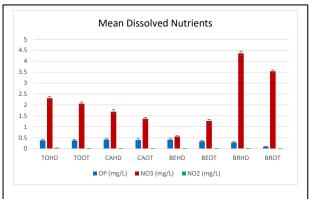
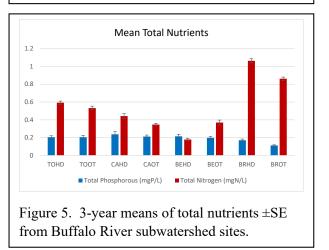


Figure 4. 3-year means of dissolved nutrients ±SE from Buffalo River subwatershed sites.



(Hernández et al. 2016) and impacts to biodiversity are found at the local, regional, and global scales (Rockström et al. 2009). A recent freshwater mussel study in the Buffalo River cited increased nitrogen at the headwaters of the Buffalo River and decreased concentrations downstream in the main river (Pieri, 2022). The sources of nitrogen in this system are largely unknown as they may result from overland flow in pastured areas, throughout the karst system emerging in springs, or within the hyporheic zone where low dissolved oxygen transforms it to ammonia.

#### 4. Lessons Learned

As indicated from the results of the three years of monitoring in the subwatersheds of the Buffalo River, only a few parameters within various watersheds is of concern. Tomahawk Creek had consistently low TSS and turbidity values. Three-year means of all TSS and turbidity values were increased by isolated stormwater events. Removing a single value from April 29, 2021, reduced the TSS and turbidity three-year means for all sampled sites. Events such as these increase the overall load into the Buffalo River and also tend to have scouring effects within the tributaries of the river. Although it is often difficult to sample during these conditions, including data from these events is vital to get the full picture of the subwatersheds.

The subwatershed with the greatest pasture land, Bear Creek, was the only subwatershed in which the TSS increased from headwater to downstream. All other TSS and turbidity values decreased from upstream to downstream in the sampled subwatersheds. Three-year mean NO<sub>2</sub> values tended to be low in these the sampling sites. However, nitrogen values, which can be of concern to sensitive aquatic species tended to be high throughout the Brush Creek Subwatershed. Thus, monitoring nitrogen values in this sensitive subwatershed should continue to include sampling for NO<sub>2</sub>. Brush Creek headwaters (BRHD) was often dry with no alternative sampling site, but some data is absent for that site.

## 5. Technical Transfer

Results from this data are part of Patrick Dyer's thesis with an anticipated graduation date of December 2023. He will be using GIS to model these watersheds to determine the impact of pasture land and riparian buffers on the water quality results in this study. These data have also been presented at local, regional and national/international meetings including the Arkansas Soil & Water Conservation meeting, Create@AState, MidSouth SETAC, SETAC North America and Young Environmental Scientists (YES) meeting. All data will be published in peer-reviewed publications. Published data are lacking in current literature that report water quality information from this economically-valuable watershed supporting unique fisheries. All data from this three-year project has been entered into WQX and thus is available through that website.

## 6. EPA Feedback Loop

To provide a complete assessment of this study and the biological surveys performed, data will be available in publications, WQX, and MS thesis at A-State. Data analyses will be available through these publications. Aquatic community assessments are also important in providing and protecting natural habitat to protect our waterways for other aquatic life and recreation, especially in the Buffalo River, the first US National River.

#### 7. Conclusions / Outcomes

This project monitored changes in water quality parameters over a three-year period. During this time, various flow and weather regimes were sampled. The overall goal is to reduce non-point source contamination and supply these data to identify subwatersheds needing additional monitoring and BMP implementation on pasture land, especially those adjacent to streams. Measurements at the headwaters and outlets of these subwatersheds provides indications of those with notable measured values adding to the contaminant load in the Buffalo River.

TSS and turbidity were lowest in the Tomahawk Creek Subwatershed. All subwatersheds had lower mean turbidity at the outlet sampling site and all had lower mean TSS values at the outlet site with the exception of Bear Creek. The most drastic reduction in mean TSS and turbidity values was in Brush Creek. However, Brush Creek (BRHD and BROT) had the greatest mean NO<sub>3</sub> and Total N of all sampling sites, although there was a decrease in nitrogen values from BRHD and BROT, values still remained greater than those measured at any other sampling site. Terrain slope may have resulted in nitrogen transport into Brush Creek and further modeling of the watershed could be performed to locate pasture land contributing nitrogen to the stream. Other sources that could be investigated include sampling the springs which contribute to Brush Creek as source water.

The increased TSS and nitrogen values in Bear Creek (BEHD and BEOT) reflect the landuse changes in the Bear Creek subwatersheds. Pasture land increased from 23-41% and forested land decreases from 72-50% from BEHD to BEOT subwatersheds, thus most likely the increased input from downstream pastures lead to in the additional TSS and nitrogen contributions at BEOT. Best management practices

in Bear Creek and Brush Creek subwatersheds should be considered to reduce input from changes in landuse.

Protection of the Buffalo River as an ecologically sensitive waterbody is important not only for economic benefits for the State, but also for biodiversity and protection of sensitive aquatic species. According to the National Park Service, the Buffalo National River annually supports 1.5M visitors who contribute \$66M in economic benefits to the state (NPS, 2021). Balancing public access and protection of the river system is vital for Arkansas' economy and sustaining the biodiversity of this unique river system.

## 8. References

ADEQ. 2018. Arkansas Department of Environmental Quality. 2018 Integrated water quality monitoring and assessment report. Prepared pursuant to sections 305(b) and 303(d) of the Federal Water Pollution Control Act.

APHA. 2005. Standard methods for the examination of water and wastewater. 21st ed. American Public Health Association, Washington D.C.

Bouldin, J.L., Farris, J.L., Moore, M.T., Cooper, C.M. 2004. Vegetative and structural characteristics of agricultural drainages in the Mississippi Delta landscape. Environmental Pollution 132: 403-411.

Hernández, D.L., Vallano, D.M., Zavaleta, E.S., Tzankova, Z., Pasari, J.R., Weiss, S., Selmants, P.C., Morozumi, C. 2016. Nitrogen Pollution Is Linked to US Listed Species Declines. BioScience 66:213–222. https://doi.org/10.1093/biosci/biw003.

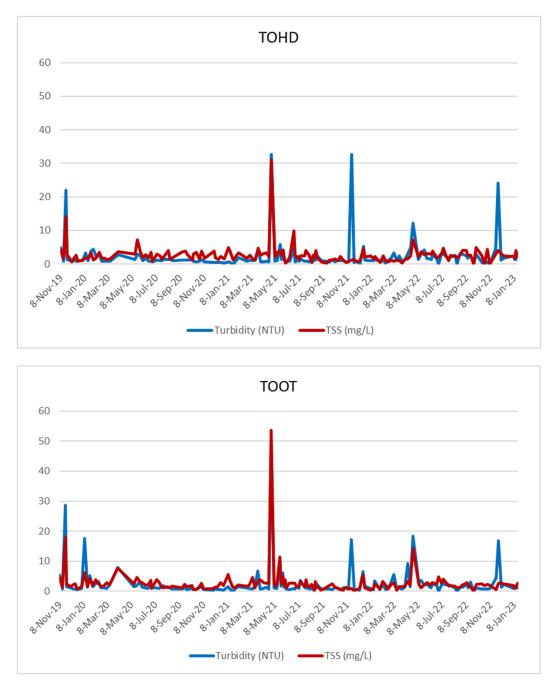
National Park Service (NPS). 2021. Tourism to Buffalo National River Creates \$66 Million in Economic Benefits. https://www.nps.gov/buff/learn/news/tourism-to-buffalo-national-river-creates-66-million-in-economic-benefits.htm#:~:text=Harrison%2C%20Arkansas%20%E2%80%93%20A%20new%20National, local%20economy%20of%20%2476.1%20million.

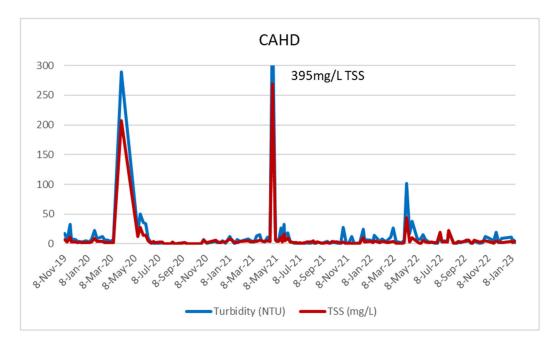
Rockström, J., Steffen, W., Noone, K. et al. 2009. A safe operating space for humanity. Nature 461: 472–475. https://doi.org/10.1038/461472a.

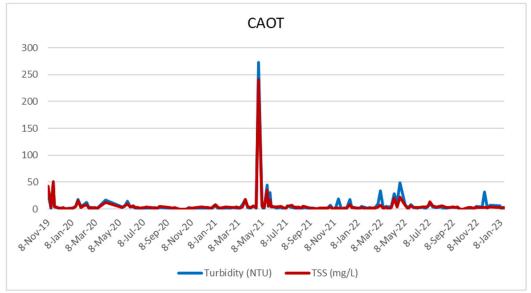
Singh, S., Coppi, L., Wang, L., Tenuta, M., Holländer, H.M. 2019. Regionalisation of nitrate leaching on pasture land in Southern Manitoba. Agricultural Water Management (222) 286-300.

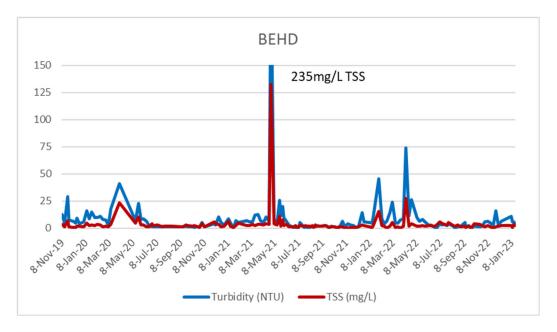
# Appendix 1.

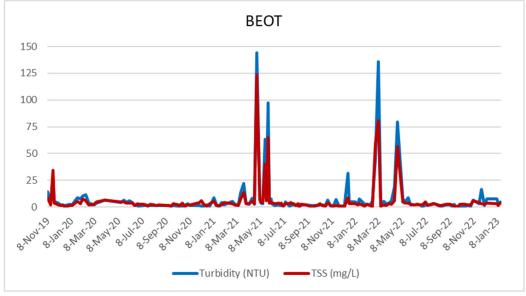
Turbidity and TSS figures for subwatersheds in the Buffalo River. Figures for headwater and outlet from each subwatershed reflect the same scale for ease of comparison.

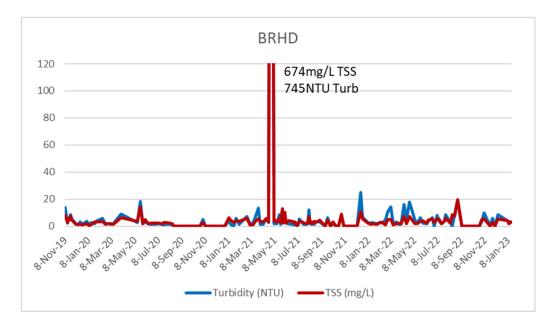


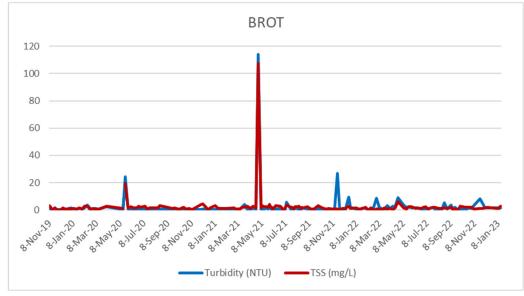






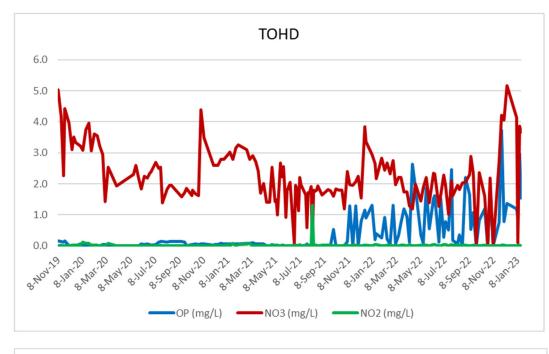


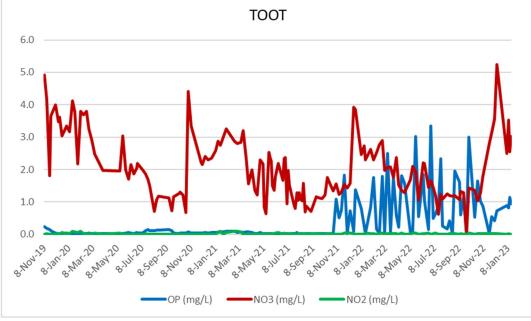


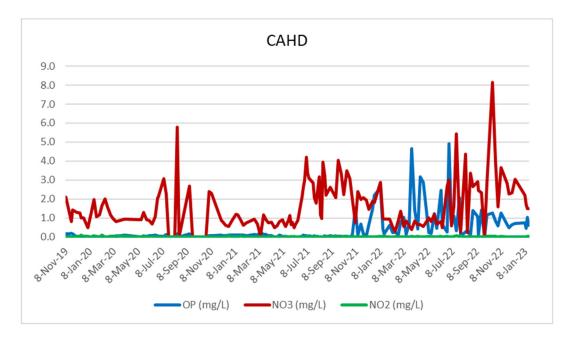


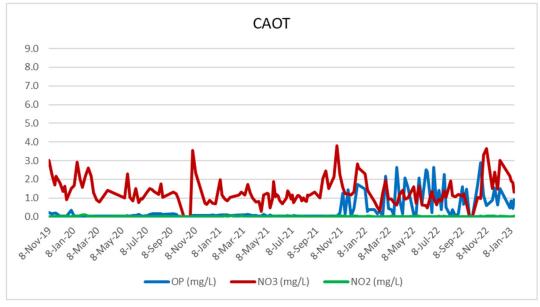
# Appendix 2.

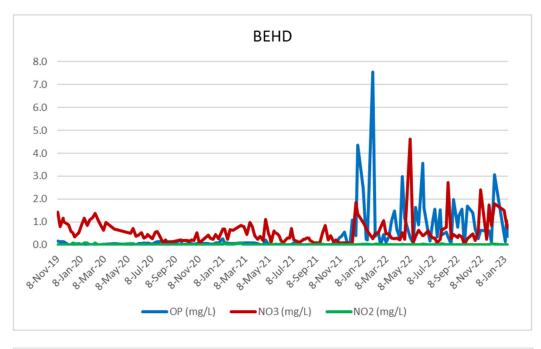
Dissolved nutrient figures for subwatersheds in the Buffalo River. Figures for headwater and outlet from each subwatershed reflect the same scale for ease of comparison.

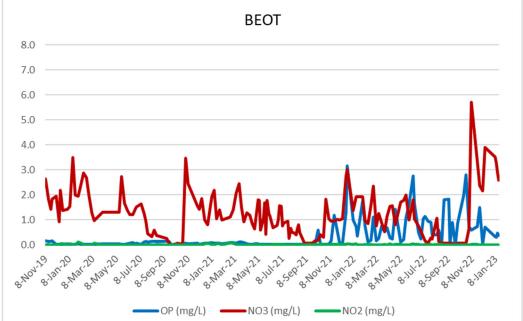


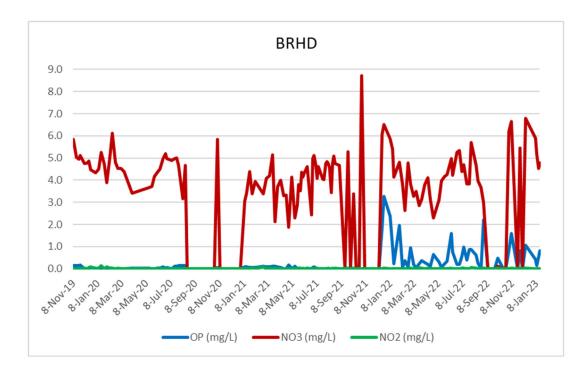


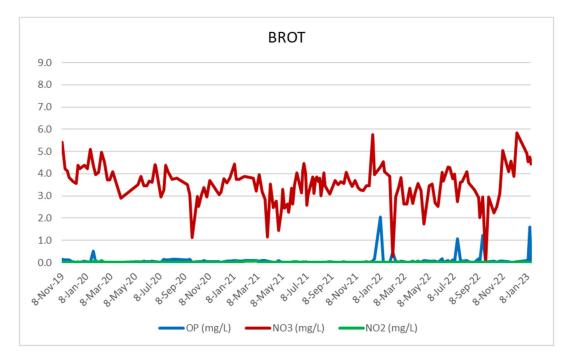






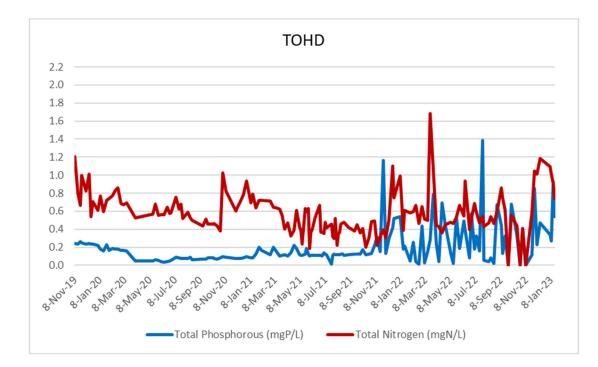


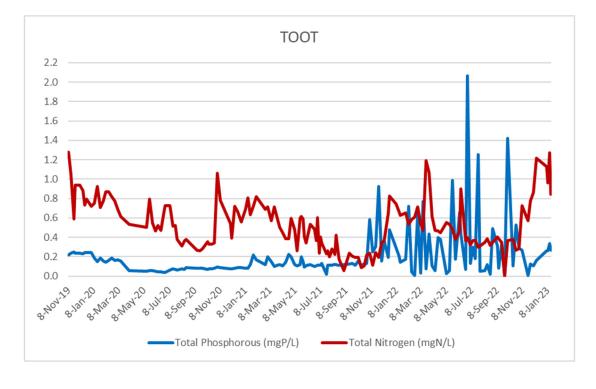


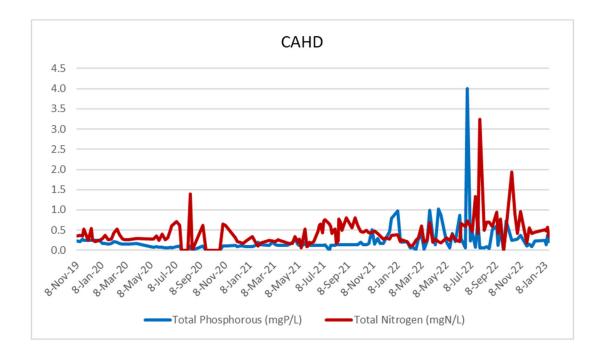


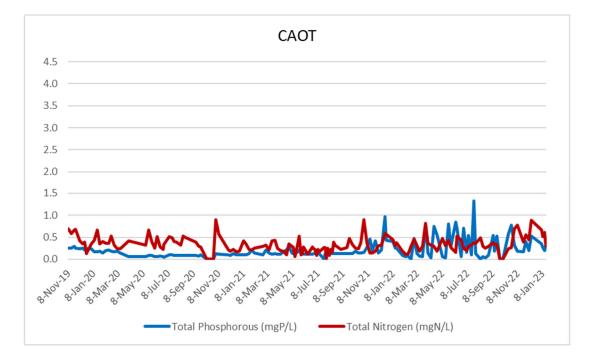
# Appendix 3.

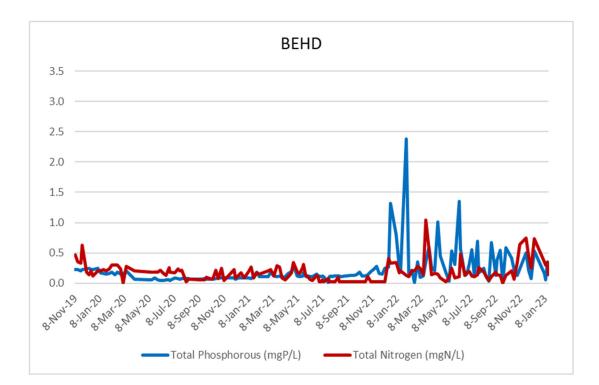
Total P and N figures for subwatersheds in the Buffalo River. Figures for headwater and outlet from each subwatershed reflect the same scale for ease of comparison.

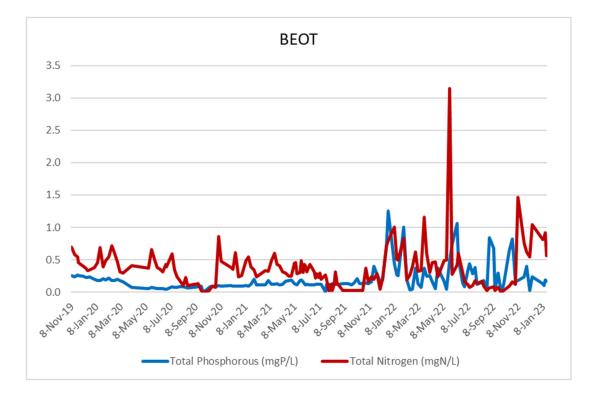


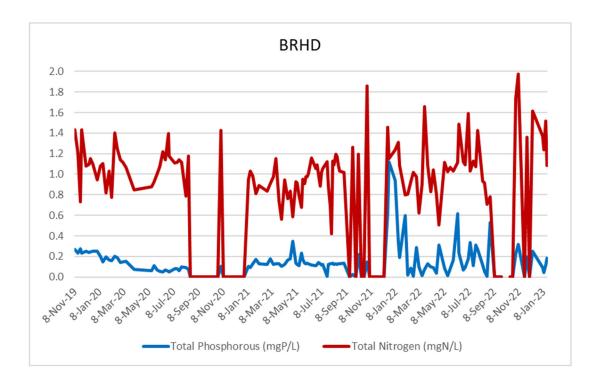


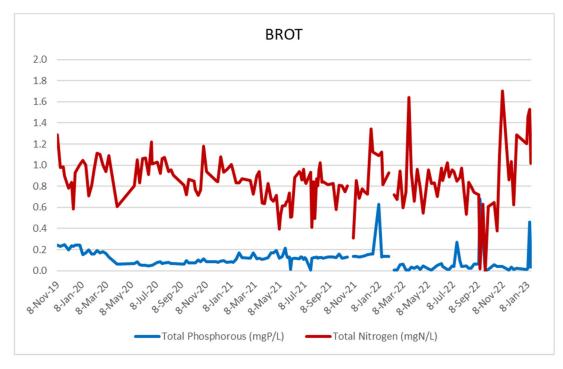












# Appendix 4.

Excel spread sheet of all measured water quality parameters.