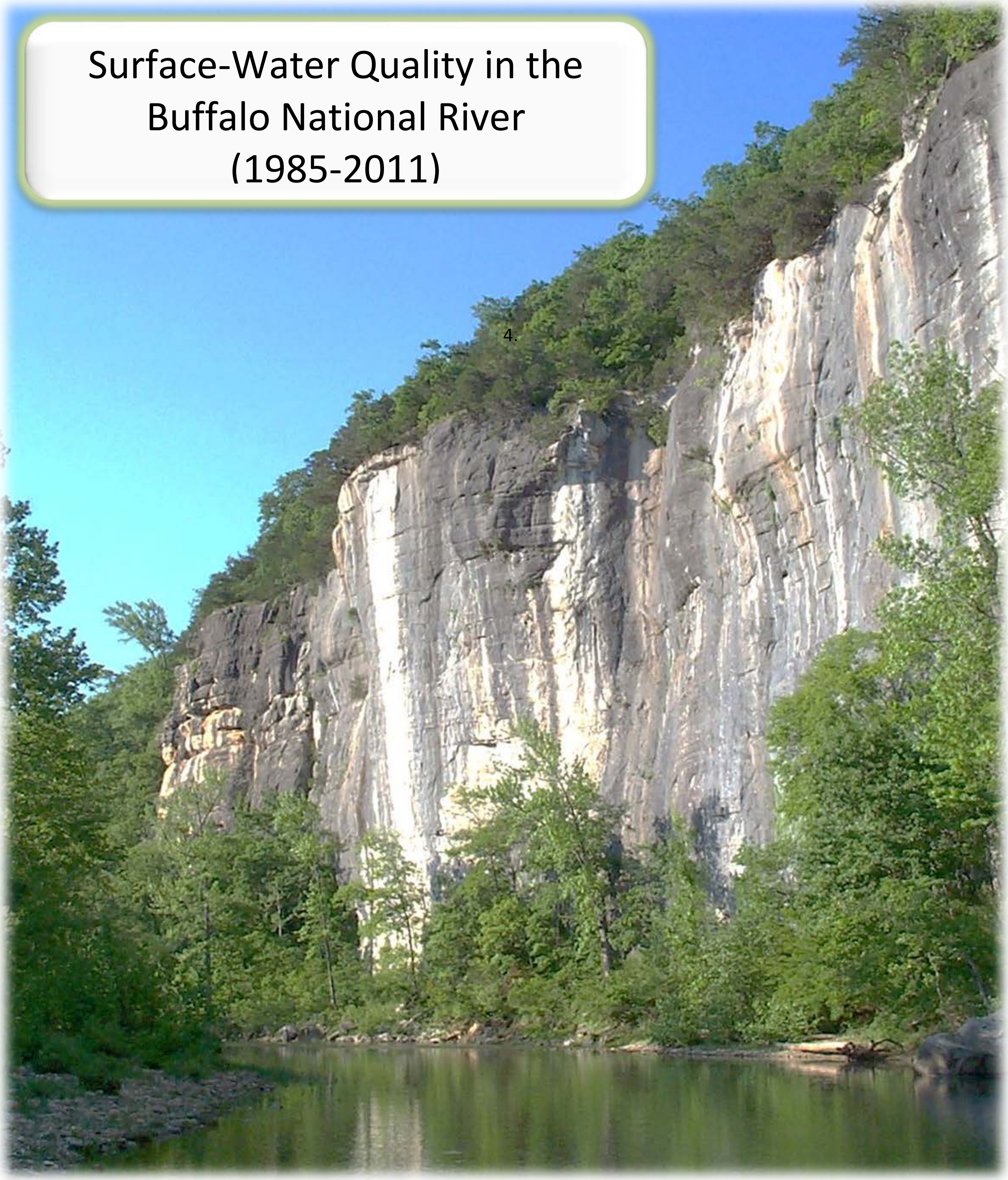
Surface-Water Quality in the Buffalo National River (1985-2011)



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Executive Summary

The Buffalo River is a 150-mile long free-flowing river located in north-central Arkansas that traverses Newton, Marion, Baxter, and Searcy Counties. The Buffalo River was designated by Congress as the country's first National River in 1972 (Public Law 92-237). This act created the Buffalo National River (BNR), a park consisting of 132 miles of the Buffalo River and nearly 100,000 acres surrounding the river.

Water quality monitoring of the BNR by the National Park Service began in 1985 to provide information that can be used to help protect this Extraordinary Resource Water (as designated by the Arkansas Pollution Control and Ecology Commission) and its major tributaries for terrestrial and aquatic biota and current and future visitors and future generations. The historical data provide a baseline of water quality conditions of the BNR, so that degradation in water quality can be recognized and addressed. The purposes of this report are to (1) describe the water quality of the Buffalo River and several of its tributaries within the BNR between 1985 and 2011, with a focus on data collected between 1995 and 2011; (2) compare selected data from 1995 through 2011 (hereafter 1995-2011) with data collected from 1985 through 1994 (1985-1994) and from 1991 through 1998 (1991-1998) that was evaluated in previous BNR water quality studies; and (3) compare the water quality to pertinent water quality standards. To date, there have been two previous statistical reviews of the data provided by the BNR water quality monitoring program (see the discussion in section 1.3).

Water quality data for 9 sites along the river corridor and 20 sites on tributaries were summarized by site, site type, and year in section 4 of this report. Water quality data were summarized for fecal coliform bacteria, nitrate, orthophosphate, turbidity, dissolved oxygen, water temperature, pH, specific conductance, sulfate, chloride, sulfate, fluoride, and alkalinity. Selected water quality data also were summarized for three springs.

Water quality is affected by land use. Concentrations of fecal coliform bacteria, nitrate, and orthophosphate generally increased with increasing percentages of pasture. During base-flow conditions, R02 (Ponca) continues to have the highest geometric mean and mean fecal coliform concentrations when compared to the other river corridor sites. The geometric mean fecal coliform concentration at R02 is approximately three times higher than the mean of the geometric means of the other eight river corridor sites. A dense area of agricultural lands is adjacent to the Buffalo River between R01 and R02 and is primarily used to support cattle operations. Tomahawk Creek (T14) was the only tributary to exceed 14 col/100 mL with a geometric mean concentration of 39.7 col/100 mL. Only a small part of T14's watershed is within the park boundary, and pasture land is closer to the river than most other sampling sites. Correlation analysis showed that tributary-site fecal coliform bacteria concentrations increased with increases in percent pasture land within each watershed. A positive correlation was shown between mean nitrate concentrations of all samples collected at each river corridor site and the percent pasture land within the upstream watershed. A similar correlation was shown between mean nitrate concentrations of all samples collected at each tributary site and the percent pasture land within the upstream watershed. Mean orthophosphate concentrations at river corridor sites during base-flow conditions did not vary substantially and ranged from 0.007 to 0.009 mg/L. The highest mean concentrations were associated with the four sites in the most-downstream section of the Buffalo River. Mean orthophosphate concentrations at tributary sites often were higher than at the river corridor sites and exceeded 0.030 mg/L at T10 (Calf Creek) and T13 (Brush Creek).

Water quality also is affected by geology. Specific conductance and alkalinity increased in a downstream direction because of the increasing influence of the carbonate geology (Mott, 1997). Mean turbidity was highest at sites in the upstream part of the watershed because there is more underlying sandstone and shale and less groundwater contribution in that area (Mott, 1997).

Dissolved oxygen concentrations seldom exceeded Regulation 2 water quality standards. Dissolved oxygen concentrations exceeded the standard 30 times—most frequently at tributary sites. Values of pH never exceed the standard.

Water temperature infrequently (35 of 493 measurements at river corridor sites and 9 of 1,135 measurements at tributary sites) exceeded the water quality standards. However, more than half of all measurements (31 of 60) made during June through August at river corridor sites in the Ozark Highlands exceeded the standard. Few exceedances of water temperature occurred at the river corridor in the Boston Mountains or at tributary sites.

Several recommendations were made (see section 5.2 of this report) and are summarized in this paragraph. A 'Buffalo River Watershed (BRW) Planning Team' that includes representation of all stakeholders, i.e. landowners, industry, agriculture-based operations, government agencies, non-governmental organizations such as watershed groups and others, should be formed to discuss and help to implement the recommendations in this report. Best management practices and other programs should be implemented to reduce erosion, runoff from cattle operations, and gravel roads in Boxley Valley and Tomahawk Creek. Inadequately treated wastewater associated with outdated package plants and septic tanks in the Mill Creek watershed (T04) should be addressed immediately to address concerns related to bacteria and nutrients. A program should be developed through the BRW Planning Team to work with both Ponca and Mill Creek landowners to upgrade individual treatment systems (septic tank and leach fields) and outdated package plants to improve waste water treatment by incorporating better quality septic systems or newer and better technology. Other areas with similar problems in the watershed should be identified and addressed. The need for development and implementation of additional BMPs at a large swine concentrated animal feeding operation (CAFO) in the Big Creek watershed should be evaluated. The effects of potential changes in stream geometry on water temperature exceedances of state water quality standards should be evaluated.

Introduction

1.1. Description of Buffalo National River

The Buffalo River is a 150-mile long free-flowing river located in north-central Arkansas that traverses Newton, Marion, Baxter, and Searcy Counties. The Buffalo River was designated by Congress as the country's first National River in 1972 (Public Law 92-237). This act created the Buffalo National River (BNR), a park consisting of 132 miles of the Buffalo River and nearly 100,000 acres surrounding the river. The BNR is managed by the U.S. Department of Interior's National Park Service (NPS). The river begins in the Boston Mountains approximately 15 miles southwest of Boxley, Arkansas near Fallsville, and winds its way through the Ozark Highlands generally flowing eastwardly to its confluence with the White River at Buffalo City, Arkansas (Figures 1.1.1 and 2.1.1). Unique natural features including multi-colored bluffs, caves, springs, sinkholes, waterfalls, and grand rock formations can be found throughout the BNR (Figure 1.1.2). Both locals and visitors treasure these extraordinary qualities of the river, its corridor, and its expansive wilderness. These qualities make the BNR an incredible resource as a scenic, natural area and as a source of tourism income to the local communities.

The NPS states that the "purpose of the Buffalo National River is to preserve, conserve, and interpret a clear, clean, free-flowing river and its Ozark mountain setting of deep valleys, towering bluffs, wilderness, and pastoral landscapes. It is not one single quality, but the combination of natural, scenic, cultural, and scientific features that are protected for the benefit and enjoyment of present and future generations" (National Park Service, 2015). The Arkansas Pollution Control & Ecology Commission (APC&EC) designated the Buffalo River an Extraordinary Resource Water and a Natural and Scenic Waterway (Arkansas Pollution Control and Ecology Commission, 2015) due to its beautiful aesthetics and exceptional recreational value.

The BNR receives approximately 1.2 million visitors per year that tour local highways and primitive roads, camp, canoe, fish, and swim (Stynes, 2011). The park has 17 concessioners that rent canoes, kayaks, rafts, and johnboats; there are also many other private operations such as lodges, cabins, restaurants, bed and breakfasts, and stores that service the needs of the public visiting the BNR. Cui and others (2013) state that visitors spent an estimated 38.2 million dollars in the local economy, contributing 468 jobs with a payroll estimated at 10.4 million dollars. Approximately 88% of the spending was by non-local visitors.

Over one million visitors come to the park to canoe, swim, or kayak the river. Visitors tend to travel in groups when floating the river and their day use of the river averages five to six hours (Davenport and Smith, 2007). If people stay longer than six hours, this generally results in an overnight stay, typically by camping or finding off-site accommodations, such as hotels, motels,

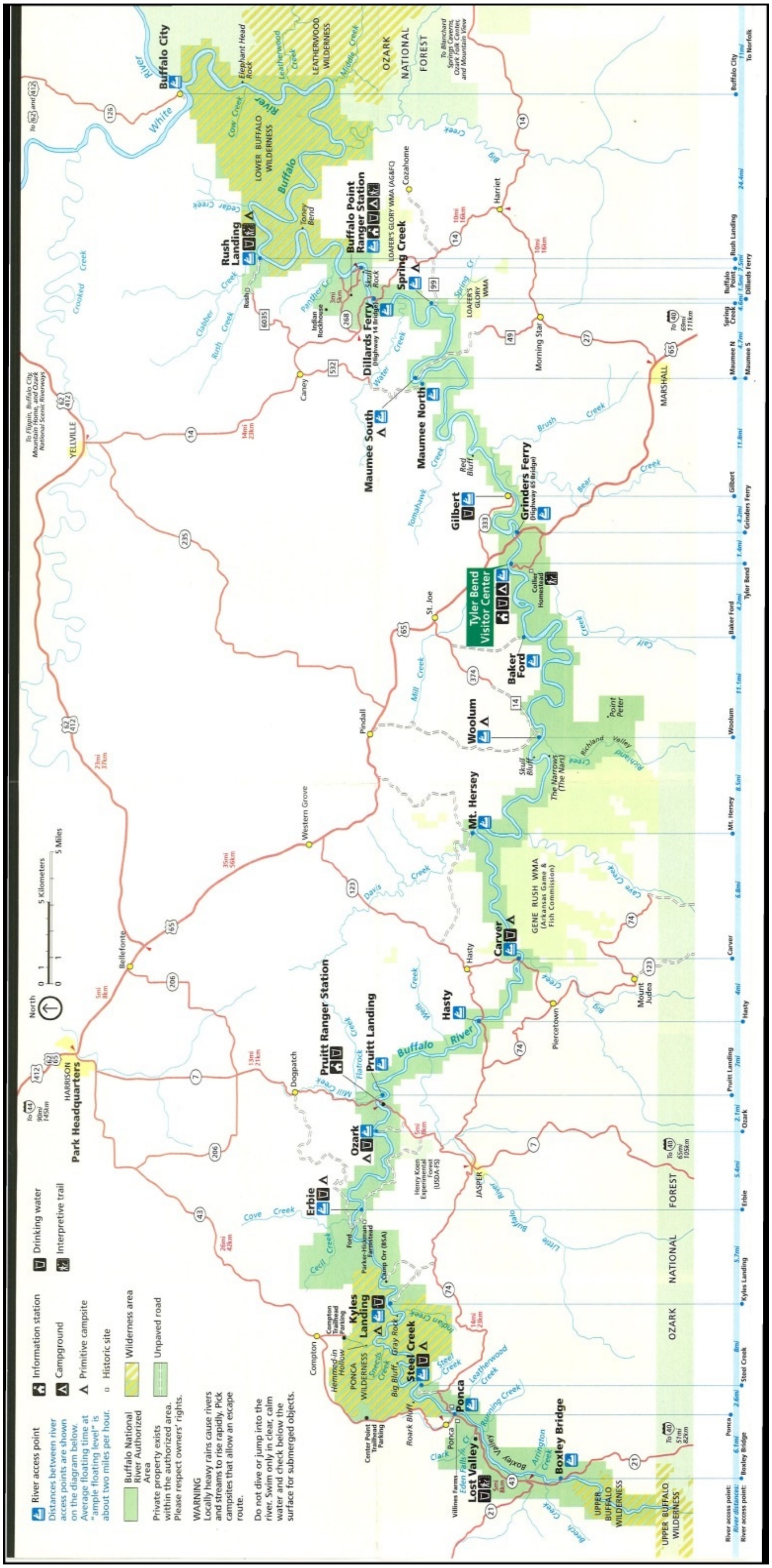

Figure 1.1.1 Buffalo National River (map courtesy of National Park Service)

and bed and breakfasts. The most popular reaches of the river are from Steel Creek to Kyles Landing, Tyler Bend to Gilbert, and Dillards Ferry to Rush Landing. Use patterns follow seasonal water levels with early spring use occurring mainly in the upstream reaches of the river and summer use occurring mainly in the middle and lower reaches of the river as water levels decline.

Figure 1.1.2 The Buffalo River is treasured for its unique rock formations and other natural features found throughout the river corridor and watershed

1.2. Purpose and Objectives of Water Quality Sampling and Report

Water quality monitoring of the Buffalo River by the NPS began in 1985 to provide information that can be used to help protect this Extraordinary Resource Water and its major tributaries for terrestrial and aquatic biota and current and future visitors and future generations. As an Outstanding National Resource Water (40 CFR 131.12(a)(3)) and an Extraordinary Resource Water (Arkansas Pollution Control and Ecology Commission, 2015), anti-degradation policies described in Regulation 2 (Arkansas Pollution Control and Ecology Commission, 2015) and 40 CFR 131.12(a)(3) require that existing instream water uses and the level of water quality necessary to protect the existing uses shall be maintained and protected. Water quality data collected were compared to current Arkansas state water quality standards to evaluate compliance; data were not analyzed using the water quality assessment methodology of the Arkansas Department of Environmental Quality (2016). The historical data provide a baseline of water quality conditions of the Buffalo River, so that degradation in water quality can be recognized and addressed. The ongoing water quality monitoring directly contributes to the primary objective of the BNR (Mott, 1997).

The purposes of this report are to (1) describe the water quality of the Buffalo River and several of its tributaries within the BNR between 1985-2011, with a focus on data collected at 9 corridor sites and 20 tributary sites (see tables 3.1.1 and 3.1.2 for a list of site IDs and site names) between 1995-2011; (2) compare selected data from 1995-2011 with data collected from 1985-1994 or from 1991 through 1998 (these selected time-frames are based on previous BNR water quality studies discussed in section 1.3); and (3) compare the water quality to pertinent water quality standards.

BNR water quality data were analyzed statistically to investigate potential trends that may indicate changes resulting from in-stream use and anthropogenic effects of land uses in the watershed. Samples were categorized as samples collected when the river flow was not recently influenced by storm-water runoff (base-flow samples) and when the river flow was influenced by storm-water runoff conditions (storm-flow samples). Several different types of analyses were applied for comparison to the two previous BNR studies. Water quality was examined by comparing means, geometric means, and other statistical metrics to current State water quality standards (Arkansas Pollution Control and Ecology Commission, 2015), by comparing differences between sample sites, and by comparing values over time. Water quality data for fecal coliform bacteria, nitrate, orthophosphate, turbidity, dissolved oxygen, water temperature, pH, specific conductance, sulfate, chloride, fluoride, and alkalinity are described.

1.3. Previous Buffalo National River Water Quality Studies

To date, there have been two previous statistical reviews of the data provided by the water quality monitoring program. The first was titled "Buffalo National River, Arkansas, Ten Years of Water Quality Monitoring" (Mott, 1997). Mott (1997) reported on water quality monitoring on the Buffalo River and its tributaries from 1985-1994. This report evaluated base-flow and storm-flow water quality and compared results to State water quality standards. The second study was "Water Resources Management Plan, Buffalo National River, Arkansas" (Mott and Luraas, 2004). This study included a comprehensive evaluation of water resources within the Buffalo River watershed. It included an evaluation of water quality based on monitoring data from 1991 through 1998. Additionally, the report included a study on fish communities in the Buffalo River together with an evaluation of the fluvial geomorphology and anthropogenic changes that have influenced the stream morphology. The results of water quality monitoring from both of these studies are compared to the data presented in this report.

1.4. Emerging Issues

1.4.1. Effects of Regional Climate Change

The climate of the Buffalo River watershed is characterized by long, hot summers and relatively short, mild winters. Monthly normal (mean from 1981-2010) temperatures at Harrison ranged from 38.1 °F in January to 78.4 °F in July (National Centers for Environmental Information, 2016). The greatest amounts of precipitation occurred in April (monthly normal of 4.32 inch), May (4.69 inch), and June (4.24 inch). July (3.14 inch) and December through January (2.56 to 3.20 inch) are the driest months. Runoff varies widely by season. Dry river sections are common in late summer and fall, except in the lower reaches, where floatable conditions are usually maintained for the entire year. Both moderately intense local storms and storms with heavier rainfall can last several days (National Park Service, 2003). Larger storms are more likely to occur in spring; however, they can occur anytime during the year. The growing season is 200 days annually, which would indicate that vegetative recovery from impacts of construction or overuse would be fairly rapid on good soils (Natural Resources Conservation Service, 1995).

Effects of accelerated global climate change caused by anthropogenic activities on the Buffalo River's ecosystem are unknown. A recent evaluation of ambient air temperatures in and near the Buffalo River watershed region indicated an increase of 2° C (about 4 °F) over the past 50 years in mean August and January temperatures (Hodges, 2012). These observations in temperature fluctuation could be part of a natural oscillation cycle within the regional environment; however, if these temperature increases intensify or lengthen as a result of climate change, impacts to the aquatic fauna's species densities and composition may be dramatic. Fifty years covers many generations for most aquatic organisms, but increases in thermal stress may far outpace any short-term gains in localized adaptations. Most certainly, increased ambient temperatures will have a direct impact on water quality, fauna distributions and species compositions, and the surface and groundwater hydrology of the river (Shawn Hodges, National Park Service, personal communication, February 2016).

1.4.2. Effects of Evolving Agricultural Practices

Land use in many parts of the Ozark Highlands and Boston Mountains and in some parts of the Buffalo River watershed includes pasture for production of cattle and poultry (Mott and Luraas, 2004). Water quality in areas with higher percentages of pasture generally differs (nutrient and bacteria concentrations higher in areas with higher percentages of pasture) from water quality in areas with higher percentages of forest (Petersen and others, 1998). However, existing agricultural practices may evolve in the area.

Evolution toward vertical integration (combination of multiple production stages into one company) of agriculture, particularly in the meat industry is another issue that is likely to have long-term impacts upon the water quality of the Buffalo River and its tributaries (Shawn Hodges, National Park Service, personal communication, February 2016). In 2013, a large swine concentrated animal feeding operation (CAFO) was established near Big Creek (T06) about 5 miles upstream from the confluence with the Buffalo River. The waste management system for this CAFO consists of spreading liquid manure and bio-solids on 16 fields in the immediate area. Environmental and conservation groups and the NPS are concerned about the potential buildup of phosphorus, nitrogen, and other constituents of hog waste and potential negative impacts upon groundwater, Big Creek, and the Buffalo River (Buffalo River Watershed Alliance, 2016). In the past 20 years, several small swine operations and dairy farms were operating in the watershed but most have ceased operations. This particular CAFO is larger than all the swine operations combined that were operating in the watershed in 2013. Meat consumption around the world is expected to increase, resulting in an increase in the vertical integration of meat production to achieve economies of scale. Areas of lower human population and poor soils will continue to be targeted for this type of operation. It is plausible that additional operations may be developed within the watershed and potentially impact groundwater, the river, and its tributaries (Shawn Hodges, National Park Service, personal communication, February 2016).

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2. Watershed Characteristics

2.1. Ecoregions

The Buffalo River watershed lies within two ecoregions, the Ozark Highlands and the Boston Mountains. The western and southern parts of the watershed lie in the Boston Mountains, while the north-central and eastern parts of the watershed lie in the Ozark Highlands (Figure 2.1.1). The Buffalo River begins in the Boston Mountains ecoregion approximately 20 miles southwest of Ponca and eventually reaches the Ozark Highlands near Gilbert. State water quality standards are based on ecoregion and the number of sampled water quality sites is divided about equally between the Ozark Highlands and Boston Mountains (Figure 2.1.1).

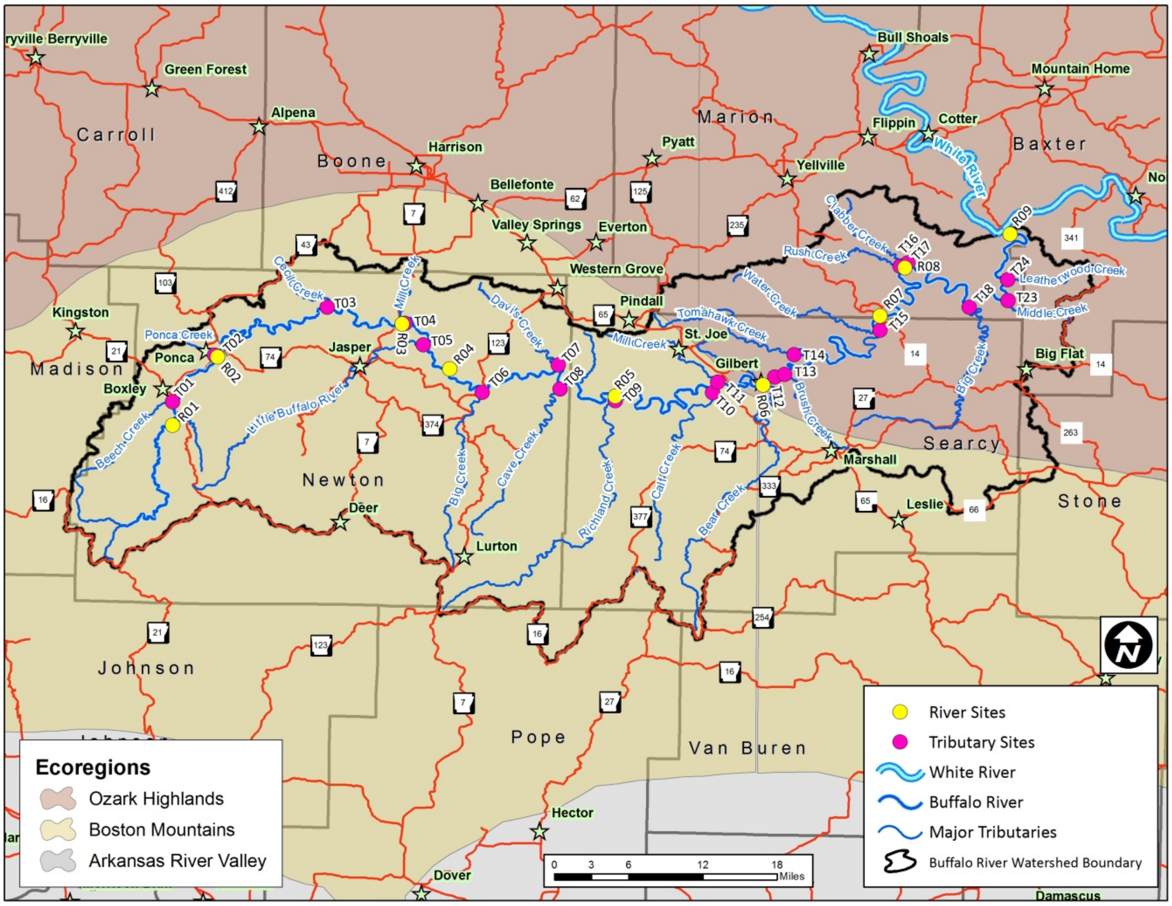


Figure 2.1.1 The Buffalo River watershed lies in the Ozark Highlands and Boston Mountains ecoregions.

The Ozark Highlands includes the Springfield and Salem Plateaus, which are underlain predominantly by highly soluble and fractured limestone and dolomite. These carbonate rocks host abundant karst features, including caves, sinkholes, losing streams, and a subsurface drainage network, which result in interconnection of surface water and groundwater. Clear, cool, perennial, spring-fed streams with gravelly substrate are common, but dry channels also occur in areas where the surface water enters the subsurface through solutionally enlarged fractures, insurgences, sinkholes, and other karst-related features.

The Boston Mountains is mountainous, forested, and underlain by Pennsylvanian-age sandstone, shale, and siltstone. Water quality of streams in this area generally is exceptional (Giese and others, 1987). During low flow, streams run clear, but during high flow, turbidity generally is high. Summer flow in small streams generally is low or nonexistent except for pools (Giese and others, 1987).

2.2. Watershed Geology

The geology of the Buffalo River watershed varies substantially, with the greatest difference being between the Ordovician through Mississippian rocks of the Ozark Highlands and the Pennsylvanian rocks of the Boston Mountains. A general description of the geology (based primarily on summaries from Adamski and others, 1995; Mott and Luraas, 2004; and Kresse and others, 2014) follows.

The rocks of the Buffalo River watershed are entirely sedimentary. They were deposited in near-shore and shallow marine basins during the Ordovician, Silurian, Devonian, Mississippian, and Pennsylvanian periods of the Paleozoic Era. The sedimentary sequence is punctuated by numerous unconformities where deposition ceased for a time and erosion occurred, to be followed by more deposition. The rocks have been subjected to erosional and tectonic forces and have developed many sinkholes, surface irregularities, fractures, and faults. These fractures and faults were further modified by erosion and dissolution processes of both surface water and groundwater

The Ordovician through Mississippian rocks host a complex karst terrain where losing streams, sinkholes, springs, and caves dominate much of the landscape. Most of these rocks are carbonates, either limestone or dolomite. They are particularly susceptible to dissolution. These rocks are highly permeable to the movement of groundwater. Subsurface flow directions and rates of groundwater flow are difficult to predict and may rapidly change based upon the hydrologic events. The river valley downstream from Boxley is entirely within this section of the sedimentary sequence (Haley and others, 1993).

The Pennsylvanian rocks are composed primarily of sandstones, shales, and siltstones. The Pennsylvanian sediments form the Boston Mountains and are found mainly within the upper reaches of the river and its southern tributaries. These rocks are much less permeable to the movement of groundwater than are the Ordovician through Mississippian rocks.

2.3. Watershed Soil Composition

The Buffalo River watershed is known for well-drained, gravelly soils and steep slopes. In the Boston Mountains, the Enders, Linker, Mountainburg, and Nella soil series are the most common. The Enders series includes deep, well-drained, and slowly permeable soils located on gently sloping to steep mountainsides. Generally, the Linker series is found on mountain tops, and is composed of moderately permeable soils that are also deep and well-drained. The Mountainburg series is located on mountaintops, mountainsides, ridges, and benches. With slopes up to 60%, these soils are shallow, well drained, and moderately to rapidly permeable. The deep, well-drained, moderately permeable Nella series can be found on mountainsides, hillsides, foot slopes, and benches. It also can have slopes up to 60% (U.S. Department of Agriculture, 1988). The Clarksville, Nixa, and Noark series occur in the Springfield Plateau and are cherty in nature. The Clarksville series is found mainly on hillsides with slopes ranging from 20% to 50%. These soils are deep, somewhat excessively drained, and moderately rapidly permeable. The Nixa series occurs on ridgetops and consists of deep, moderately well-drained, very slowly permeable soils with 3% to 12% slopes. The Noark series includes deep, moderately well-drained soils that are moderately permeable and located on gently sloping to steep hillsides and ridgetops (U.S. Department of Agriculture, 1988). Most soils contain substantial amounts of coarse fragments (predominantly chert) at the surface and in the profile (Natural Resources Conservation Service, 1995).

Much of the watershed has moderately steep land slopes. Over 73% of the watershed has land slopes greater than or equal to 7%. Nearly 47% of the slopes are between 7% and 14%; nearly 28% of the slopes are greater than 14% (Scott and Hofer, 1995). Valley slopes can be as low as 1%. Conversely, hillsides can have slopes as high as 60%. These steep slopes limit the amount of agricultural activity and land clearing associated with forest harvesting or urban development that can occur in the watershed. Activities on steep slopes can result in increased erosion of soils. Soils in pastures on steeper slopes are difficult to manage, and the use of farm equipment is restricted by the Natural Resources Conservation Service, which recommends that slopes over 15% should not be cleared for pasture (Natural Resources Conservation Service, 1995).

During their 27-year analysis period (1965-1992) study, Scott and Hofer (1995) showed the greatest loss of forest was in the two highest slope categories. More than likely, the valleys were probably cleared for pasture initially when people began to settle in the watershed. Later, as the logging industry declined, more land was cleared to create pasture to support new cattle operations, which, over time, brought income into the area. This has resulted in steeper forested slopes being converted to pastures. A more extensive presentation on the watershed soils can be found in Mott and Luraas (2004).

2.4. Land Use Evaluation

The Buffalo River watershed (1,340 mi^2) is predominantly undeveloped with approximately 81.7% of land use consisting of forest/woodland, 15.5% agriculture/grass (often referred to as “pasture” in the rest of this report), and 2.8% comprised of water, barren land, urban, and roads. (See Appendix 1, for land use analysis methods.) Agricultural land use is not evenly distributed, with a larger proportion of cleared land in the middle part of the watershed on the Boone Formation (Panfil and Jacobson, 2001). Land-use and drainage areas upstream of each designated sampling site were calculated for both the river corridor (R01-R09) and tributary (T01-T16) sites shown in Figure 2.1.1. The upstream area of the Buffalo River watershed is less developed as evidenced by the decreasing percentage of forest/woodland and increasing percentage of agriculture/grass as the river flows from R01 to R09. The drainage area of the most upstream sampling site, R01 (Wilderness Boundary), consists of 93.6% forest/woodland and only 4.5% agriculture/grass while the drainage area of the most downstream site, R09 (Mouth), consists of 81.7% forest/woodland and 15.5% agriculture/grass. A summary of drainage area and land use for all river corridor sites is shown in Table 2.4.1. Figure 2.4.1 is a map of the drainage area for site R01. The other river corridor site maps showing drainage areas can be found in Appendix 1.

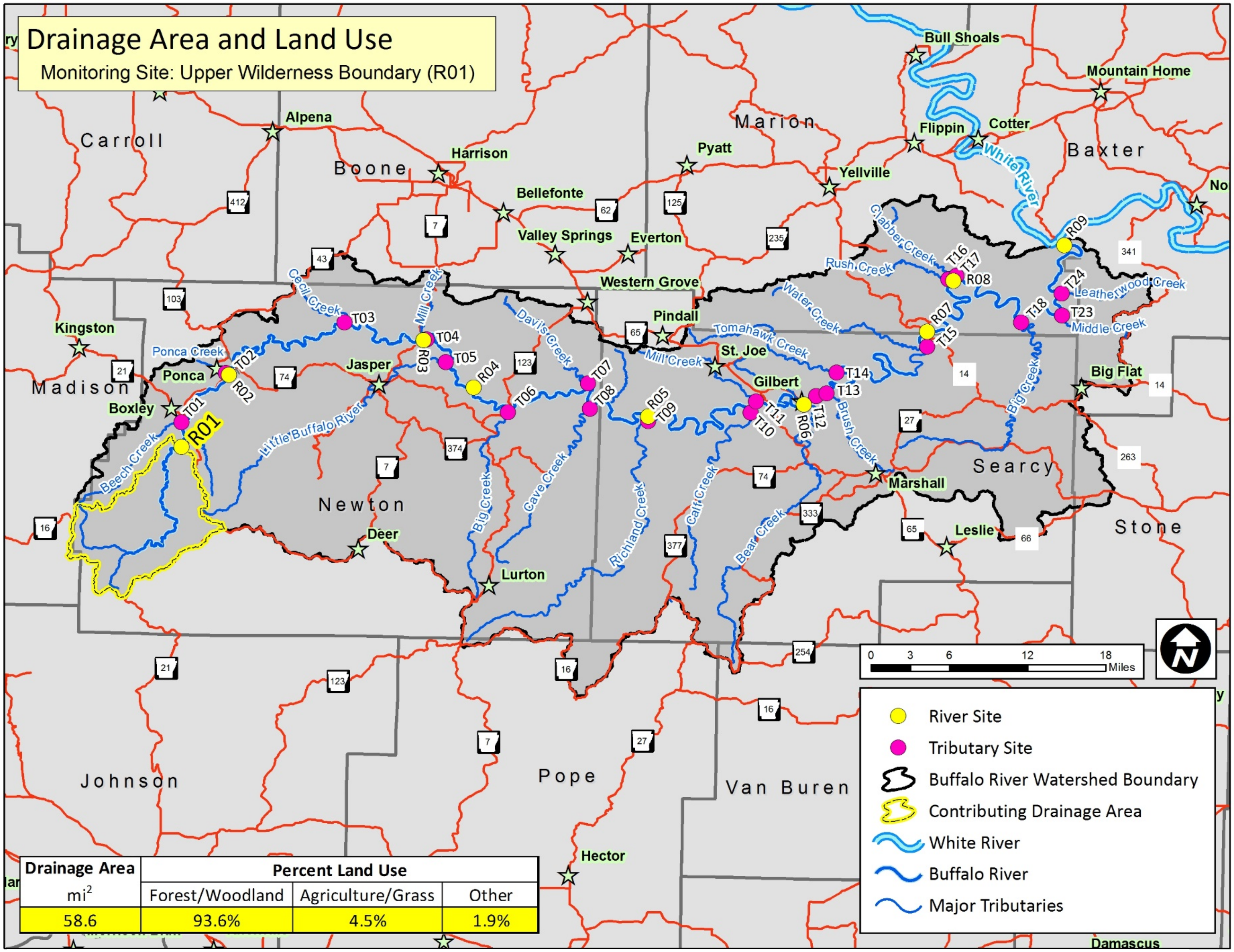
Drainage areas and land use for Buffalo River tributaries are quite variable. Forested area ranges from as high as 98.7% at T23 (Middle Creek) to as low as 66.1% at T14 (Tomahawk Creek). Tributaries discharging to the middle and lower middle section of the Buffalo River have the greatest amount of agriculture and grass lands. T18 (Big Creek-Lower) has the second largest drainage area and one of the largest agriculture/grass land-use percentages (25.3%). A summary of drainage area and land-use for all tributary sites is shown in Table 2.4.2.

Table 2.4.1 Drainage areas and land-use percentages associated with Buffalo River corridor sites percentage.

	Site ID	Drainage Area mi^2	Dominant Land Uses %		
			Forest/Woodland	Agriculture/Grass	Other
River Sites	R01	58.6	93.6	4.5	1.9
	R02	115	90.8	7.3	1.9
	R03	191	90.8	7.3	1.9
	R04	198	88.1	9.3	2.6
	R05	601	85.8	11.5	2.6
	R06	841	84.6	12.8	2.6
	R07	1071	82.0	15.2	2.8
	R08	1095	82.2	15.0	2.8
	R09	1335	81.7	15.5	2.8

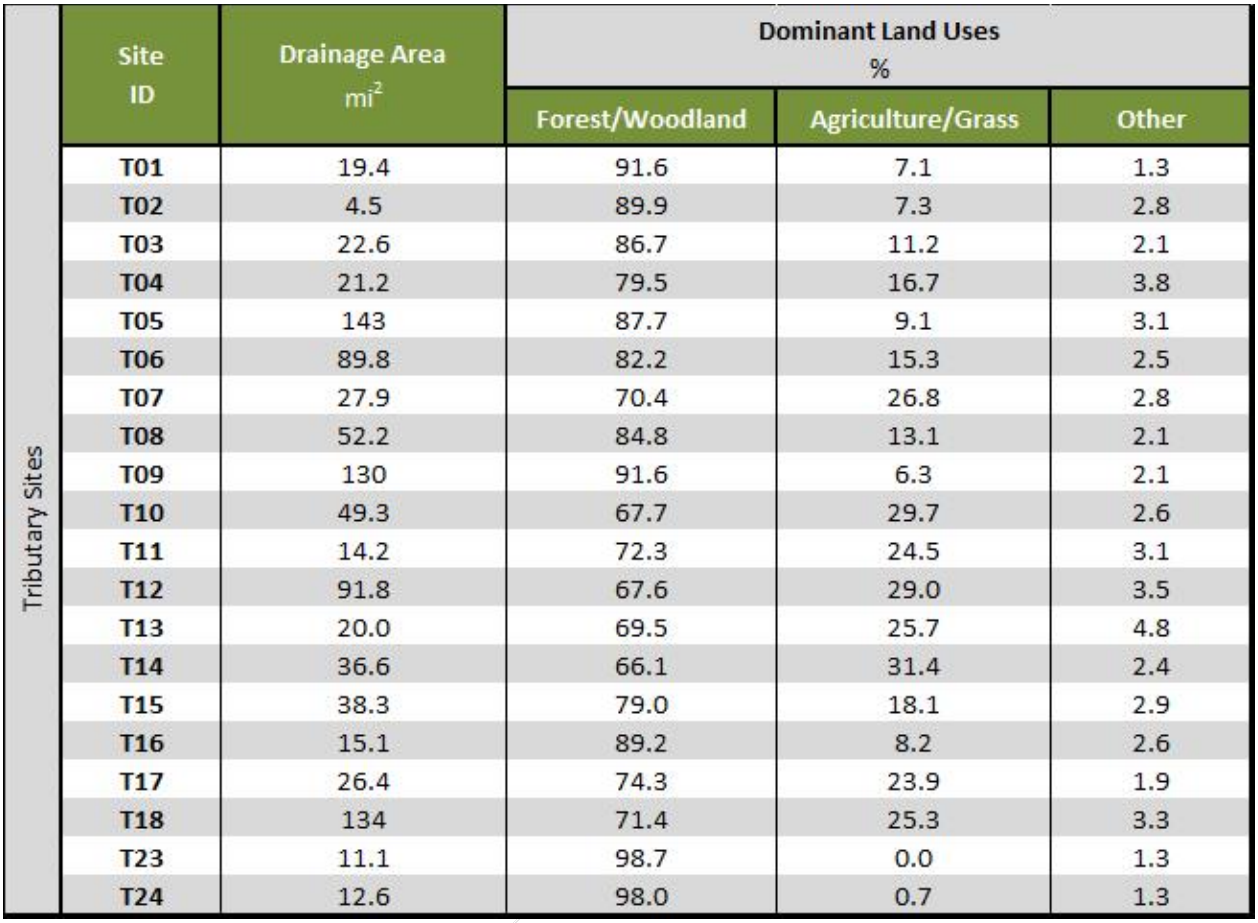
A map of the Tomahawk Creek (T14) watershed is shown as an example of the calculations employed for individual tributary watersheds (Figure 2.4.2). The other maps showing drainage area for each of the tributary sites are located in Appendix 1. The contributing drainage areas are delineated based on the drainage divides (typically ridges) between individual watersheds. The listed drainage areas do not include areas across drainage divides that might contribute groundwater to streams in the watershed.

Because of karst topography and associated characteristics and the underlying carbonate rocks, interbasin transfer of groundwater from one surface water watershed to another is likely a common occurrence. An example of this occurrence is where Mott and others (2000) describe the interbasin transfer of groundwater from about 10 mi^2 of the more-agricultural Crooked Creek watershed southward across the surface water drainage divide to springs within the less-agricultural Mill Creek (T04) watershed (see map on page A1-21 in Appendix 1). Thus, surface drainage areas and associated land use percentages may not always be completely representative of the hydrology of a water quality site.



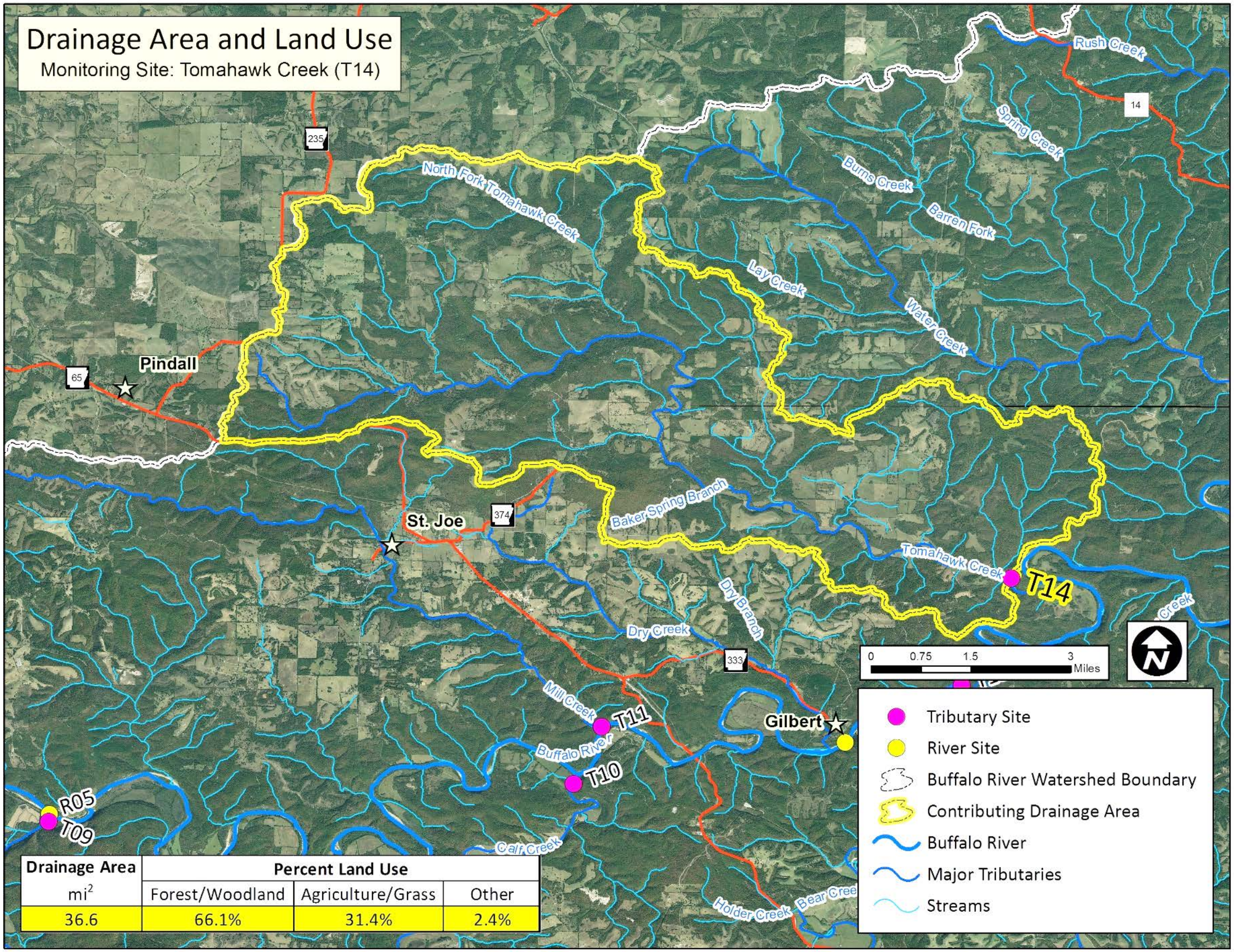
Drainage Area	Percent Land Use		
mi^2	Forest/Woodland	Agriculture/Grass	Other
58.6	93.6%	4.5%	1.9%

Figure 2.4.1 Drainage area and land-use associated with site R01 (Other river corridor site maps can be found in Appendix 1)



	Site ID	Drainage Area mi^2	Dominant Land Uses %		
			Forest/Woodland	Agriculture/Grass	Other
Tributary Sites	**T01**	19.4	91.6	7.1	1.3
	T02	4.5	89.9	7.3	2.8
	T03	22.6	86.7	11.2	2.1
	T04	21.2	79.5	16.7	3.8
	T05	143	87.7	9.1	3.1
	T06	89.8	82.2	15.3	2.5
	T07	27.9	70.4	26.8	2.8
	T08	52.2	84.8	13.1	2.1
	T09	130	91.6	6.3	2.1
	T10	49.3	67.7	29.7	2.6
	T11	14.2	72.3	24.5	3.1
	T12	91.8	67.6	29.0	3.5
	T13	20.0	69.5	25.7	4.8
	T14	36.6	66.1	31.4	2.4
	T15	38.3	79.0	18.1	2.9
	T16	15.1	89.2	8.2	2.6
	T17	26.4	74.3	23.9	1.9
	T18	134	71.4	25.3	3.3
	T23	11.1	98.7	0.0	1.3
	T24	12.6	98.0	0.7	1.3

Table 2.4.2 Drainage area and land-use associated with Buffalo River tributary sites.



Drainage Area	Percent Land Use		
mi^2	Forest/Woodland	Agriculture/Grass	Other
36.6	66.1%	31.4%	2.4%

Figure 2.4.2 Tomahawk Creek (T14) watershed area and land-use (Other tributary site maps can be found in Appendix 1)

3. Water Quality Data - Methods

3.1 Site Analysis and Sampling Locations

Water quality sampling within the Buffalo River watershed occurs at 9 sites along the river corridor, 20 sites on tributaries of the Buffalo River, and 3 springs (Figure 3.1.1). The tables below list the site names, which are based on prominent local features or waterways (Table 3.1.1, 3.1.2, 3.1.3).

For this report, the presentation of data focuses on that collected from 1995-2011. Other data dating back to 1985 are included for comparison to previous water quality studies by Mott (1997) and Mott and Luraas (2004) and to evaluate trends beginning in 1985. Data and results are shown in section 4 and appendices 2 and 3.

Table 3.1.1 Buffalo River corridor sites

River					
R01	Wilderness Boundary	R04	Hasty	R07	Highway 14
R02	Ponca	R05	Woolum	R08	Rush
R03	Pruitt	R06	Gilbert	R09	Mouth

Table 3.1.2 Buffalo River tributary sites

Tributaries					
T01	Beech Creek	T08	Cave Creek	T15	Water Creek
T02	Ponca Creek	T09	Richland Creek	T16	Rush Creek
T03	Cecil Creek	T10	Calf Creek	T17	Clabber Creek
T04	Mill Creek	T11	Mill Creek-Middle	T18	Big Creek-Lower
T05	Little Buffalo River	T12	Bear Creek	T23	Middle Creek
T06	Big Creek	T13	Brush Creek	T24	Leatherwood Creek
T07	Davis Creek	T14	Tomahawk Creek		

Table 3.1.3 Buffalo River spring sites

Springs					
S02	Luallen Spring	S33	Mitch Hill Spring	S41	Gilbert Spring

Locations for river, tributary, and spring sampling sites were selected in 1985 by scientists from the NPS's Water Resources Division and Ouachita Baptist University (Thornton and Nix, 1985). The location of sampling sites on the Buffalo River (R01-R09) were established upstream of tributary and river confluences to avoid sampling areas where tributary waters were still mixing with river water. The locations of tributary sites (T01-T24) were established at the mouth of the tributary just before the tributary converged with the Buffalo River (Mott, 1997). The purpose of sampling these sites was, and is, to provide critical water quality-data for management of the Buffalo River and its tributaries.

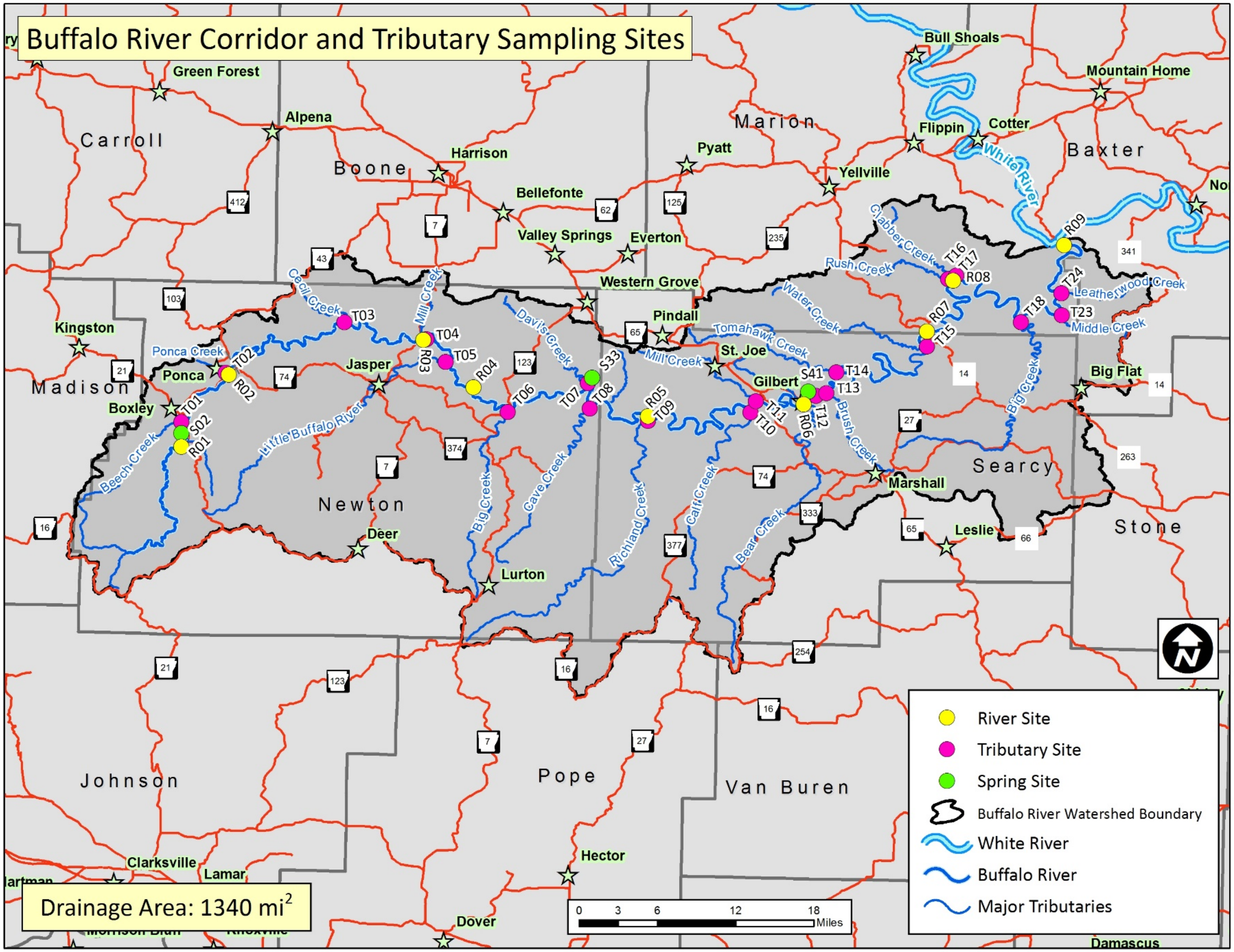


Figure 3.1.1 Buffalo River corridor, tributary, and spring water quality sites.

3.2 Sample Collection

Sampling for water quality on the Buffalo River, tributaries, and springs began in 1985. Because of the extensive period of data collection, after a baseline was established, the frequency of samples collected annually has changed over time resulting in a change in total samples collected per year. From 1985 to 1990, sampling occurred approximately once a month for river corridor sites and twice a month between May and September for tributary and spring sites; from 1991 to 1995, samples were collected six times per year in alternating months. Since 1996, samples have been collected seasonally. Samples are categorized into base-flow, rising limb, or falling limb samples based upon the regional hydrograph. Base-flow samples are associated with stream flows composed of recharge from groundwater. Rising and falling limb samples are associated with storm flows and the addition of surface runoff.

3.3 Parameters and Methods for Analysis

Methods for water quality monitoring were first presented in the BNR Water Quality Plan (National Park Service, 1985), with updates and additional parameters added as needed (American Public Health Association and others, 1992; Mott, 1997). The Arkansas Department of Environmental Quality (ADEQ), (prior to 1999, known as the Arkansas Department of Pollution Control and Ecology, but will be referred to as ADEQ throughout this report) assisted with the analysis of the water quality samples. Collection of water samples was consistent with ADEQ methodologies. Samples and physiochemical measurements were collected by wading to the thalweg of the stream and collecting the sample below the water's surface, at approximately 60% of the depth when possible. Samples and measurements were collected facing upstream with care given to approach the sampling site from downstream so as to not disturb stream sediments. ADEQ provided all nutrient collection containers and oversaw all laboratory aspects of QA/QC for the water samples analyzed in the ADEQ laboratory. These water samples were delivered by chain of custody to ADEQ field staff and transported to the ADEQ laboratory for analysis. Bacteria (fecal coliform) and turbidity analysis were performed by trained water quality technicians at BNR. Bacteria and turbidity samples were collected in sterile sample containers. All sample containers were labeled with a site identifier, collection time, location, and the initials of the collector with water insoluble ink prior to collection of a sample.

The following parameters were measured *in situ*: discharge (cubic feet per second), temperature (degrees Celsius), conductivity (microsiemens per centimeter), pH, and dissolved oxygen (milligrams per liter, mg/L). The following parameters were processed in the BNR's Water Quality Laboratory: turbidity (nephelometric turbidity units) and fecal coliform bacteria (colonies per 100 milliliters). The following parameters were analyzed by ADEQ at their laboratory following United States Environmental Protection Agency (USEPA) approved methods: chloride (mg/), sulfate (mg/L), fluoride (mg/L), ammonia as nitrogen (NH_3-N; mg/L), nitrate as nitrogen (NO_3-N; mg/L), and orthophosphate as phosphorus (PO_4-P; mg/L). Other data not described in this report are available at: https://www.nps.gov/buff/learn/nature/research.htm

3.3.1. Field Measurements

Dissolved Oxygen

Dissolved oxygen (DO) is a measure of the concentration of oxygen in a liquid. In natural waters, it is dependent on biochemical oxygen demand, chemical oxygen demand, rate of atmospheric reaeration, photosynthesis, respiration, and water temperature (Mott, 1990). The minimum DO standard for streams with watershed areas ranging from 10-100 mi^2 in the Ozark Highlands is 6 mg/L for the primary season (temperature less than 22° C) and 5 mg/L for the critical season (temperature equal to or greater than 22°C); for watersheds with areas greater than 100 mi^2, the minimum DO standard is 6 mg/L (Arkansas Pollution Control and Ecology Commission, 2015). The DO minimum standard for streams with watershed areas less than 10 mi^2 and for watersheds greater than or equal to 10 mi^2 in the Boston Mountains is 6 mg/L for the primary season (temperature less than 22° C) and 2 mg/L and 6 mg/L, respectively, for the critical season (temperature equal to or greater than 22°C) (Arkansas Pollution Control and Ecology Commission, 2015). Dissolved oxygen measurements were made using the latest industrial-grade quality DO meter by placing the probe into the top 6-12 in of the stream in a well-mixed riffle. The measurements were taken and values were recorded when the device displayed a constant reading for several seconds. The meter was standardized using an air-calibration chamber prior to each collection event as prescribed in the operating manual.

pH

pH is the negative logarithm to the base 10 of the hydrogen-ion concentration of a solution. Most natural waters are buffered solutions that resist changes in pH (Chow, 1964). Most sites are located in the Springfield Plateau and have a large amount of exposed limestone within the respective watersheds, which keeps surface-water runoff well buffered. Arkansas water quality standards for pH state that pH levels must not fluctuate more than 1.0 unit in a 24-hour period and may not be above 9.0 or below 6.0 (Arkansas Pollution Control and Ecology Commission, 2015). A pH meter was used to measure this parameter at the time of sample collection. The pH meter was standardized with two pH buffer solutions (7 and 10) prior to each collection event and then checked regularly against a standard to ensure proper calibration.

Specific Conductance and Water Temperature

Specific conductance is the ability of water to conduct an electrical current. Specific conductance is dependent on the concentration of ions in solution, the charge of those ions, and the temperature of the water. Because conductance is temperature dependent, it is reported at a standard temperature of 25 degrees Celsius; i.e., specific conductance. Probes for measurement of specific conductance and temperature were placed directly in the upper 6-12 inches of the stream for measurements. The conductivity meter was calibrated with appropriate solutions prior to each collection event. The meter automatically compensates for temperature and displays specific conductance directly.

3.3.2. Buffalo National River Laboratory Measurements

Turbidity

Turbidity detracts from the aesthetic qualities of a stream and is defined as the ability of suspended and colloidal materials to diminish the penetration of light (Chow, 1964). The regulation for turbidity is that "there shall be no distinctly visible increase in turbidity of receiving waters attributable to discharges or instream activities". For the Ozark Highlands and the Boston Mountains, a value of 10 NTU "…should not be exceeded during base flow (June to October) in more than 20% of samples" and values of 17 NTU (Ozark Highlands) and 19 NTU (Boston Mountains) "…should not be exceeded during all flows in more than 25% of samples taken in not less than 24 monthly samples" (Arkansas Pollution Control and Ecology Commission, 2015).

Turbidity samples have a 72-hour holding time, and samples were analyzed with a HACH 2100A turbidimeter at the BNR Water Quality Field Laboratory. The meter was calibrated prior to analysis using the appropriate range of standards for the predicted turbidity values.

Fecal coliform bacteria

Analysis for fecal coliform bacteria followed the Membrane Filtration Method—9222.D (American Public Health Association and others, 1992), which allow a 6-hour maximum holding time between collection and incubation (American Public Health Association and others, 1992). Due to the relatively short holding time, it was necessary to perform fecal coliform bacteria analyses at the BNR Water Quality Laboratory. Blank samples were analyzed with each sample to ensure there was not sample contamination during the filtering process.

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4. Water Quality Data - Results

4.1 Statistical Summary of Data and Comparison to Standards

A statistical summary of base-flow data utilized in this report beginning in 1985-2011 is shown in Tables 4.1.1, 4.1.2, and 4.1.3. The arithmetic means and standard deviations of water quality data of the Buffalo River corridor, tributaries, and springs for the parameters in Tables 4.1.1, 4.1.2, and 4.1.3 are compared to Arkansas water quality standards. The results show that these values do not exceed the values used in water quality standards; however, arithmetic means and standard deviations cannot be directly compared to water quality standards from a regulatory perspective, but this analysis can be useful to evaluate the water quality data collected at river corridor, tributary, and sites.

Table 4.1.1 Arkansas water quality standards and Buffalo River corridor base-flow sample statistics

[col/100 ml, colonies per 100 milliliters; NTU, nephelometric turbidity units; N/A, not applicable; mg/L, milligrams per liter; C, Celsius; µS, microsiemens; mi^2, square miles]

Parameter	Period of Record	Number of Samples	Mean	Standard Deviation	Current Standard[1] Boston Mountains Ecoregion	Ozark Highlands Ecoregion
Fecal coliform bacteria (col/100 mL)	1985-2011	1148	16	66	200 - 400	
Turbidity (NTU) base/all flow	1988-2011	949	1.98	2.02	10[2]/19[3]	10[2]/17[3]
Nitrate, as nitrogen (mg/L)	1985-2011	792	0.087	0.114	N/A	
Orthophosphate, as phosphorus (mg/L)	1999-2011	269	0.007	0.010	N/A	
Chloride (mg/L)	2003-2011	233	2.63	0.93	20	
Sulfate (mg/L)	2003-2011	232	5.04	1.12	20	
Dissolved oxygen (mg/L)	1985-2011	1016	9.88	2.11	Primary season > 6 Critical season >6[5]/2[4]	 >6 >6[7]/5[6]/2[4]
Water temperature (°C)	1985-2011	1164	17.8	10.5	31	29
pH	1999-2011	361	8.02	0.35	6-9	
Specific conductance (µS/cm at 25 °C)	1985-2011	1158	180	64	N/A	
Alkalinity, as $CaCO_3$ (mg/L)	2003-2011	232	96	29	N/A	
Fluoride (mg/L)	1985-2011[8]	416	0.061	0.025	N/A	

[1] ***Arkansas Pollution Control and Ecology Commission (2015)***

[2] ***Samples collected during base flow***

[3] ***All collected samples***

[4] ***Watershed is less than 10*** mi^2

[5] ***Watershed is greater than 10*** mi^2

[6] ***Watershed is greater than 10*** mi^2 ***and less than 100*** mi^2

[7] ***Watershed is greater than 100*** mi^2

[8] ***Samples were not taken in all years***

Table 4.1.2 Arkansas water quality standards and Buffalo River tributary base-flow sample statistics

[col/100 ml, colonies per 100 milliliters; NTU, nephelometric turbidity units; N/A, not applicable; mg/L, milligrams per liter; C, Celsius; µS, microsiemens; mi^2, square miles] *See 4.1.3 for footnotes

Parameter	Period of Record	Number of Samples	Mean	Standard Deviation	Current Standard[1]	
					Boston Mountains Ecoregion	Ozark Highlands Ecoregion
Fecal coliform bacteria (col/100 mL)	1985-2011	2262	33	133	200 - 400	
Turbidity (NTU) base/all flow	1988-2011	2025	1.64	7.48	10[2]/19[3]	10[2]/17[3]
Nitrate, as nitrogen(mg/L)	1985-2011	1547	0.220	0.242	N/A	
Orthophosphate, as phosphorus (mg/L)	1998-2011	662	0.012	0.020	N/A	
Chloride (mg/L)	2003-2011	540	3.75	1.68	20	
Sulfate (mg/L)	2003-2011	536	6.45	2.08	20	
Dissolved oxygen (mg/L)	1985-2011	1944	9.98	2.80	Primary season > 6 Critical season >6[5]/2[4]	>6 >6[7]/5[6]/2[4]
Water temperature (°C)	1985-2011	2286	17.3	6.8	31	29
pH	1999-2011	841	8.04	0.28	6-9	
Specific conductance (µS/cm at 25 °C)	1985-2011	2268	273	90	N/A	
Alkalinity, as $CaCO_3$ (mg/L)	2003-2011	537	154	50	N/A	
Fluoride (mg/L)	1985-2011[8]	933	0.065	0.024	N/A	

Table 4.1.3 Arkansas water quality standards and spring base-flow sample statistics

[col/100 ml, colonies per 100 milliliters; NTU, nephelometric turbidity units; N/A, not applicable; mg/L, milligrams per liter; C, Celsius; µS, microsiemens; mi^2, square miles]

Parameter	Period of Record	Number of Samples	Mean	Standard Deviation	Current Standard[1]	
					Boston Mountains Ecoregion	Ozark Highlands Ecoregion
Fecal coliform bacteria (col/100 mL)	1985-2011	380	26	105	200 - 400	
Turbidity (NTU) base/all flow	1988-2011	344	1.46	1.67	10[2]/19[3]	10[2]/17[3]
Nitrate, as nitrogen (mg/L)	1987-2011	288	0.662	0.399	N/A	
Orthophosphate, as phosphorus (mg/L)	2002-2011	86	0.022	0.010	N/A	
Chloride (mg/L)	2003-2011	86	4.12	1.70	20	
Sulfate (mg/L)	2003-2011	86	6.97	3.75	20	
Dissolved oxygen (mg/L)	1985-2011	328	8.82	1.41	Primary season > 6 Critical season >6[5]/2[4]	>6 >6[7]/5[6]/2[4]
Water temperature (°C)	1985-2011	383	14.2	2.0	31	29
pH	1999-2011	154	7.46	0.28	6-9	
Specific conductance (µS/cm at 25 °C)	1985-2011	383	317	91	N/A	
Alkalinity, as $CaCO_3$ (mg/L)	2003-2011	86	181	42	N/A	
Fluoride (mg/L)	1985-2011[8]	150	0.065	0.027	N/A	

[1] *Arkansas Pollution Control and Ecology Commission (2015)*

[2] *Samples collected during base flow*

[3] *All collected samples*

[4] *Watershed is less than 10 mi^2*

[5] *Watershed is greater than 10 mi^2*

[6] *Watershed is greater than 10 mi^2 and less than 100 mi^2*

[7] *Watershed is greater than 100 mi^2*

[8] *Samples were not taken in all years*

The water quality of the Buffalo River is regulated based on standards outlined in Regulation No. 2: Regulation Establishing Water Quality Standards for Surface Waters of the State of Arkansas (Arkansas Pollution Control and Ecology Commission, 2015). Water quality standards for water bodies in the State are based primarily on designated uses and then based on ecoregions, watershed size, specified river, and/or streamflow. The Buffalo River has been designated by the APC&EC as both an Extraordinary Resource Water and Natural and Scenic Waterway. For its fisheries use, the Buffalo River falls under the Ozark Highlands or Boston Mountains depending on the location. All sampling sites (Figure 2.1.1) are located on perennial streams as defined by Regulation No. 2. Summaries of water quality sampling results as shown in Tables 4.1.1, 4.1.2, and 4.1.3 were also developed for individual river corridor, tributary, and spring sites and can be found in Appendix 3.

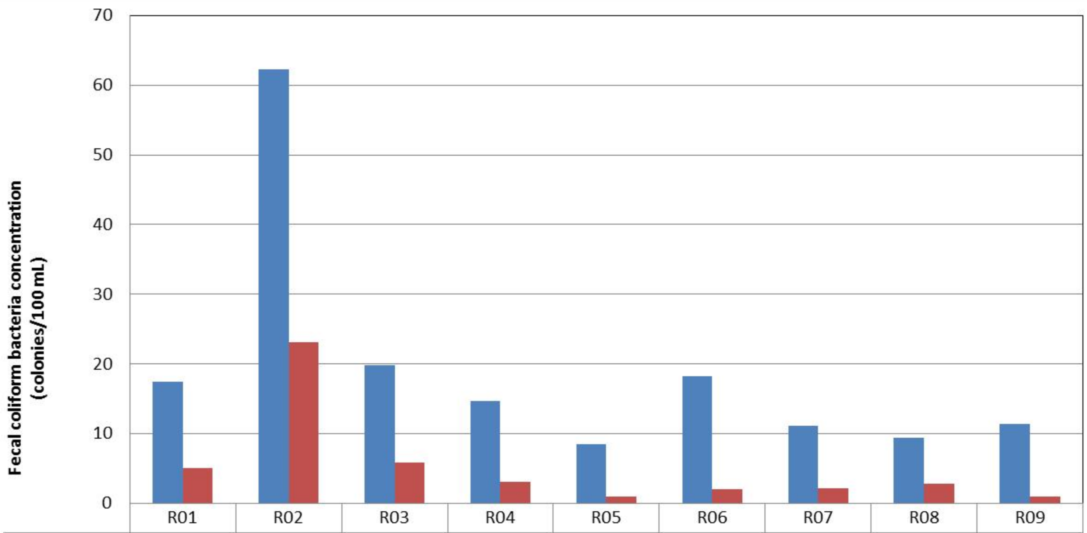
4.2 Fecal Coliform Bacteria

This section presents the results of analyses for fecal coliform bacteria. Samples were collected at the river corridor and tributary sites during base-flow and storm-flow conditions. For determination of the geometric mean, zero values were equated to 0.01 to eliminate the problem of dividing by zero.

4.2.1 Buffalo River Corridor Sites

Base-flow conditions

The arithmetic mean and geometric mean of fecal coliform bacteria concentrations were calculated for each river corridor site for the sampling period of 1995-2011 for samples collected during base-flow conditions (Figure 4.2.1). The number of samples collected at each site ranged from 51 to 59. With the exception of R02 (Ponca), the mean concentrations were less than 20 col/100 mL, and the geometric mean concentrations were less than 6 col/100mL. R05 (Woolum) had the lowest mean concentration of 8.5 col/100 mL and lowest geometric mean concentration of 1.0 col/100 mL based on 55 samples. Geometric mean concentrations were similar to those from Mott (1997) for river corridor sites from 1985-1994 (Mott 1997). R02 had the highest mean concentration (62.2 col/100 mL), which is greater than 3.1 times the second highest mean concentration of 19.9 col/100 mL at R03 (Pruitt). Also, R02 had the highest geometric mean concentration (23.2 col/100 mL), which is greater than 3.9 times the second highest geometric mean concentration of 5.9 col/100 mL at R03. This value is approximately three times the mean of the geometric mean values of the other eight sites. These are similar results to Mott (1997), where he found the difference to be 3.25 times.



	R01	R02	R03	R04	R05	R06	R07	R08	R09
🟦 Mean	17.5	62.2	19.9	14.8	8.5	18.3	11.1	9.4	11.5
🟥 Geomean	5.1	23.2	5.9	3.1	1.0	2.1	2.2	2.9	1.0
# of Samples	54	56	59	53	55	55	54	54	51

Figure 4.2.1 Geometric mean (geomean) and mean fecal coliform bacteria concentrations for Buffalo River corridor sites sampled between 1995-2011 during base-flow conditions.

Fecal coliform bacteria concentrations at Buffalo River corridor sites from 1999 (1999 was selected as the first year for this analysis because Mott and Luraas (2004) showed box plots for 1991-1998) through 2011 generally were highest at upstream sites (R01-R04) and generally were substantially lower at sites farther downstream. The median concentration at R02 (Ponca) is 26 colonies/100 mL, approximately three times higher than the mean of the median concentrations of the other eight sites (8.7 col/100 mL) (Figure 4.2.2).

Boxley Valley has experienced long-term agricultural land use for cattle operations, which are adjacent to the Buffalo River between sites R01 (Wilderness Boundary) and R02 (Ponca) (Figure 4.2.3). There are approximately 972 acres of pasture within 500 ft of the river, many of which are privately owned but within the park boundaries, along 7.7 miles of river or a mean of 126 acres per linear mile of river. The pastures primarily are used to graze cattle, though some areas are used for hay production. These pastures sometimes extend to the river and include a forested riparian buffer of 0 to 450 ft. Compared to other areas along the Buffalo River, Boxley Valley has the densest agricultural land use (mostly associated with cattle production) per mile of river adjacent to the river (Table 4.2.1). Boxley Valley also has abundant small tributaries that flow across these pastures to the river with little buffering by riparian growth. Though cattle have been fenced out of the Buffalo River, they still have access to numerous tributaries that flow across the large pastures adjacent to the river.

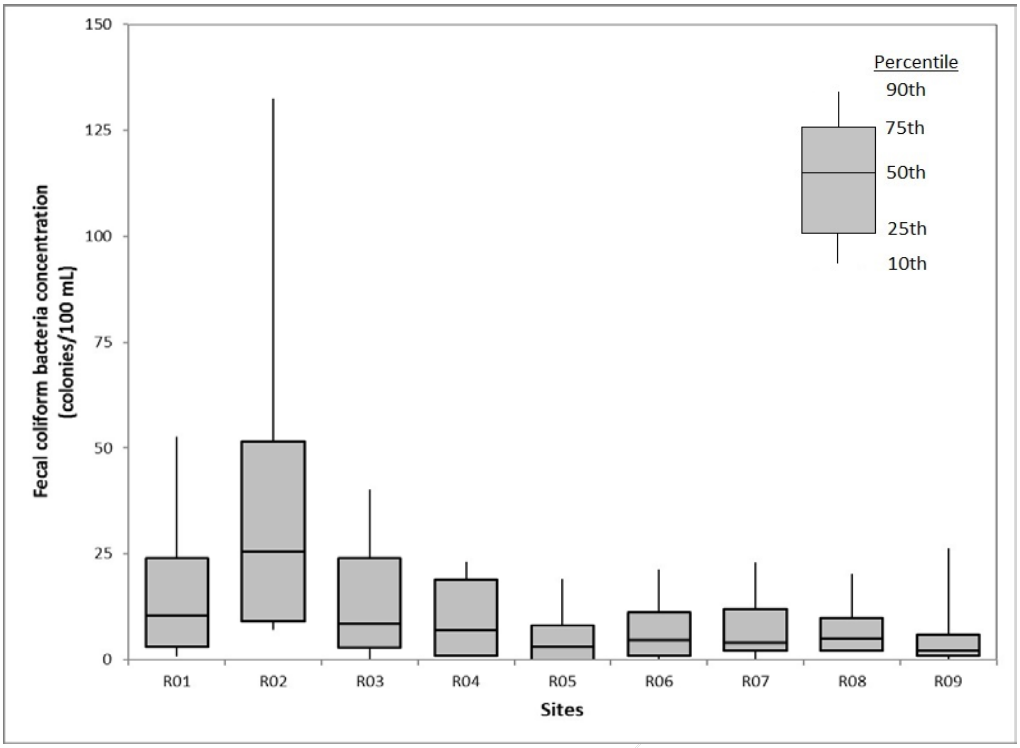


Figure 4.2.2 Fecal coliform bacteria concentrations for Buffalo River corridor sites sampled during base-flow conditions from 1999-2011.

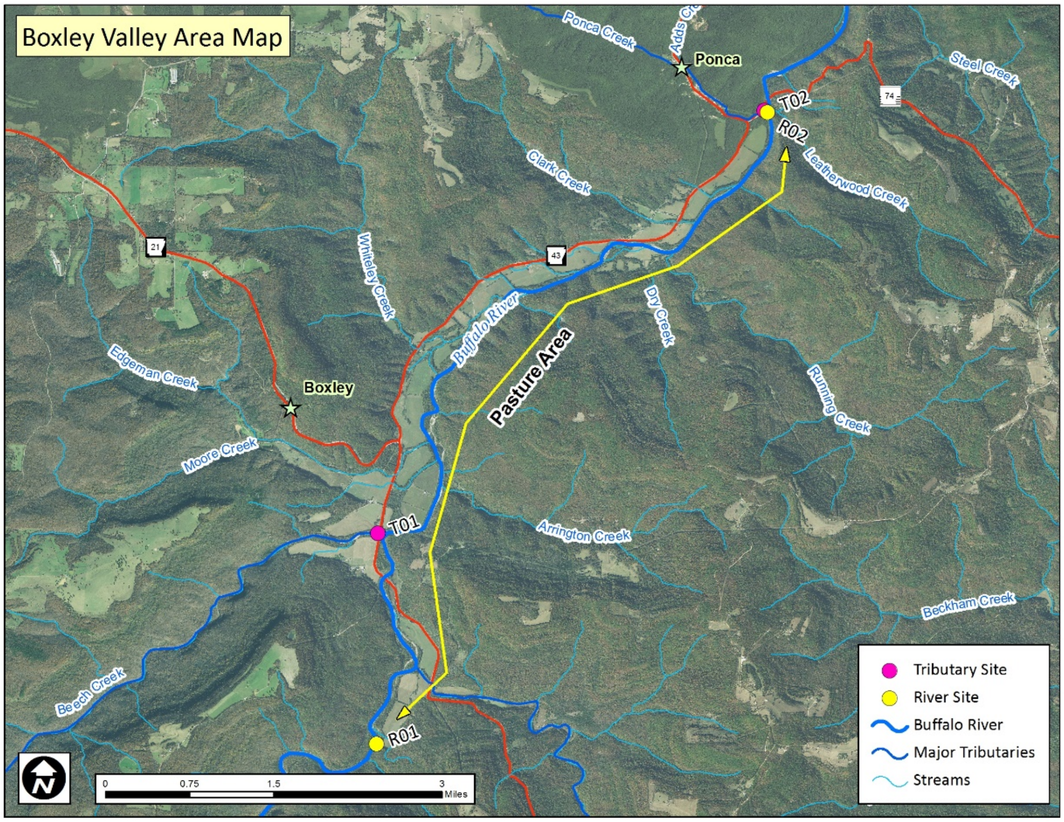


Figure 4.2.3 Location of more than 900 acres of pasture adjacent to the Buffalo River from R01 to R02 in the Boxley Valley Area.

Tributaries within fenced pasture lands have the potential to become loafing areas during the summer, where cattle are able to find water and shade. Some of these tributaries are perennial, which explains how fecal matter and nitrate from manure and urine can be transported to the river system during base-flow conditions. If these pastures are overgrazed, this can compound the problem of excessive nutrient and sediment in storm-water runoff. Elk are commonly observed in these pastures as well and can potentially contribute bacteria and nutrients.

Table 4.2.1 Acres of agriculture/grass lands adjacent to the Buffalo River between river corridor sites. [Land use was measured within a 500-foot buffer on each side of the river.]

Site Interval	Acres of Adjacent Agriculture/Grasses	Miles of River	Acres of Agriculture/Grasses Per Mile
Source-R01	0.0	13.7	0.0
R01-R02	971.6	7.7	126.2
R02-R03	224.3	23.6	9.5
R03-R04	103.7	7.3	14.3
R04-R05	224.9	19.4	11.6
R05-R06	1409.9	21.0	67.1
R06-R07	391.2	21.5	18.2
R07-R08	39.2	8.9	4.4
R08-R09	0.0	23.2	0.0

Results from the current study were similar to results associated with 1991-1998 data (Mott and Luraas, 2004). For 1991-1998 the geometric mean at R02 (Ponca) was four times higher than the mean of the geometric means of the other eight sites. Compared to Mott and Luraas (2004), the median concentration at R02 is lower (previously 28 colonies/100 mL) and the mean of the other eight medians is higher (previously 7 colonies/100 mL).

The geometric mean of base-flow fecal coliform bacteria concentrations was calculated for all river corridor samples for each year beginning in 1985 and ending in 2011 (Figure 4.2.4). The geometric mean concentrations ranged from 0.3 col/100 mL to 21.7 col/100 mL, with the highest geometric mean concentration occurring in 1999. Other years with higher relative concentrations were 1997, 1998, and 2008, with ranges from 8.6 to 16.1 col/100 mL. The geometric mean generally increased over time from 1985-1999, decreased through 2006, and then increased after 2006 (Figure 4.2.4).

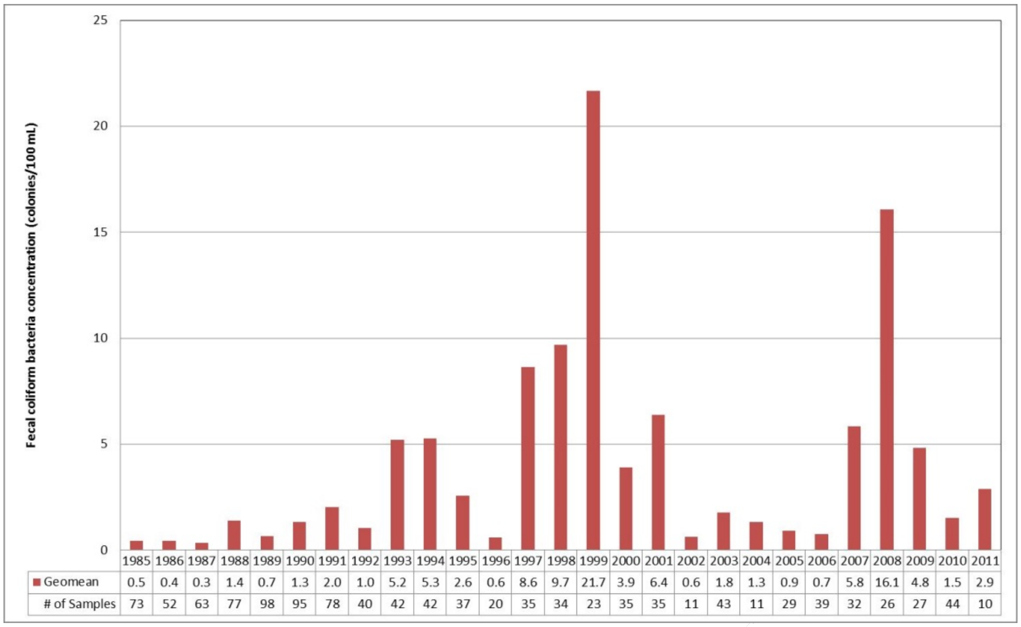


Figure 4.2.4 Annual geometric means for fecal coliform bacteria concentrations for Buffalo River corridor sites sampled from 1985-2011 during base-flow conditions.

Base flow fecal coliform bacteria concentrations do not appear to be increasing or decreasing over time from 1995-2011 (Figure 4.2.5). No statistically significant trend was detected in the 1985-1994 data (Mott, 1997).

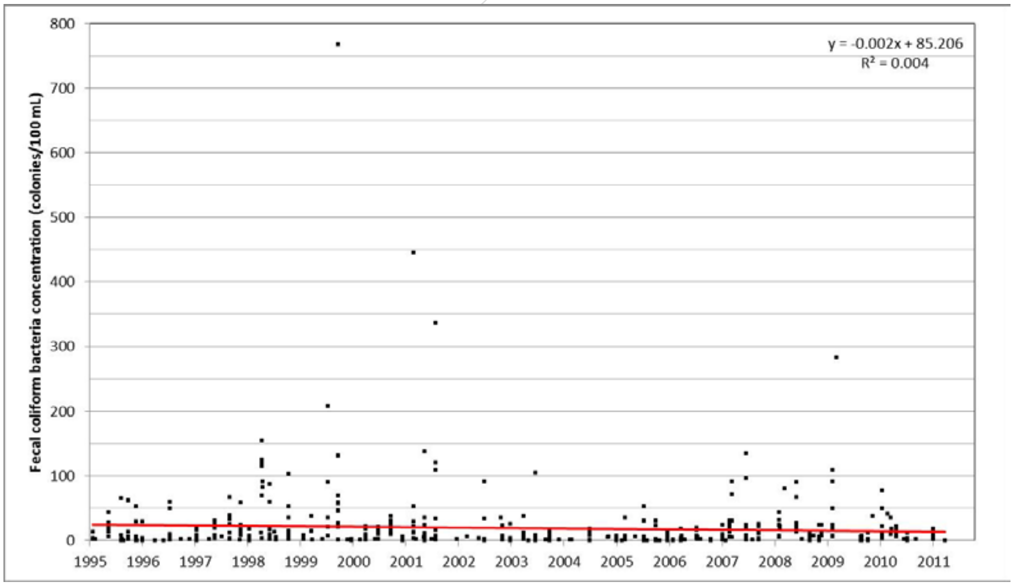


Figure 4.2.5 Fecal coliform bacteria concentrations for Buffalo River corridor sites during base-flow conditions from 1995-2011.

Although base-flow data from 1995-2011 were insufficiently frequent to make an ultimate determination, it appears that the water quality standard for fecal coliform bacteria (geometric mean of 200 col/100 mL from at least five samples during a 30-day period, or a value for an individual sample of 400 col/100 mL) for primary contact seasons was being met, except at R02 (Ponca) where two concentrations exceeded 400 col/100 mL. The water quality standard for fecal coliform bacteria for primary contact seasons (May 1 to September 30) is a geometric mean "calculated on a minimum of five (5) samples spaced evenly within a thirty (30)-day period" and an individual concentration should not exceed 400 col/100 mL (Arkansas Pollution Control and Ecology Commission, 2015)." Therefore, the sampling frequency was insufficient for determining exceedance of the geometric mean standard. However, it is important to note that concentrations for only 5 river corridor samples out of 491 collected during base-flow conditions between 1995-2011 were higher than 200 col/100 mL. Three of these five samples were collected at R02 (in 1999 and 2001) and the other two samples were collected at R06 (Gilbert) (2001) and R09 (Mouth) (2009). When evaluating the individual river corridor sites, with the exception of R02, 63% to 90% of the fecal coliform bacteria concentrations were less than 20 col/100 mL.

Storm-Flow Conditions

Grab samples (11 to 17 per site) coinciding with storm-flow events on both the rising and falling limbs of the hydrograph were collected during storm-flow conditions. Higher fecal coliform bacteria concentrations are expected during storm-flow conditions because surface-water runoff transports bacteria adsorbed to soil particles (Mott, 1990) and concentrations associated with these samples were often substantially higher than during base-flow conditions. However, variability of concentrations is very high and can be strongly affected by factors such as season, antecedent storm-flow events, rainfall duration and intensity, and position on the hydrograph (rising limb, falling limb, peak, etc.). Therefore, data from storm-flow events were not summarized.

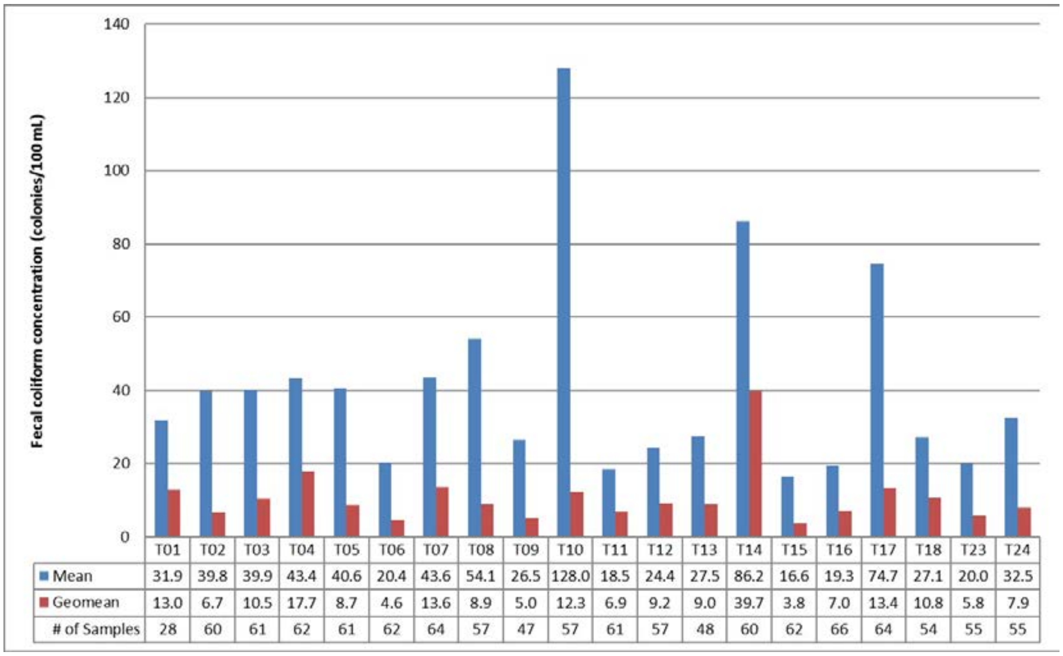
4.2.2 Tributary Sites

Base-Flow Conditions

The arithmetic mean and geometric mean of fecal coliform bacteria concentrations were calculated for each tributary site for the sampling period of 1995-2011 for samples collected during base-flow conditions (Figure 4.2.6). The number of samples collected at each site ranged from 28 to 66. The geometric means for 12 of 20 tributary sites were less than 10 col/100 mL and were similar to geometric means for most tributaries sampled in 1985-1994 (Table 4.2.2). With the exception of T10 (Calf Creek), T14 (Tomahawk Creek), and T17 (Clabber Creek), the mean concentrations were less than 60 col/100 mL; the geometric mean concentrations were less than 20 col/100mL at all sites except T14. T14 was the only tributary to exceed 20 col/100 mL with a geometric mean of 39.7 col/100 mL. A similar geometric mean of 39 col/100 ml was calculated by Mott (1997) for data collected from 1985-1994. T14 is located near the park boundary and is closer to pasture land than many other sampling sites. T15 (Water Creek) had the lowest mean concentration of 16.6 col/100 mL and lowest geometric mean concentration of 3.8 col/100 mL based on 62 samples. Geometric mean concentrations were similar to those from Mott (1997) for tributary sites from 1985-1994 (Mott, 1997). T10 had the highest mean concentration (128.0 col/100 mL). T14 had the highest geometric mean concentration (39.7 col/100 mL), which is greater than 2.2 times the second highest geometric mean concentration of 17.7 col/100 mL at T04 (Mill Creek). This value is approximately four times the mean of the geometric mean values of the other 19 sites. These are very similar results to Mott (1997), where he found the difference also to be approximately four times.

Table 4.2.2 Comparison of tributaries in which the geometric mean exceeded 10 col/100 mL from 1985-1994 and 1995-2011.

Geometric Mean Fecal Coliform Bacteria Concentrations in Tributaries (colonies/100 mL) **[Shading indicates a site with geometric means exceeding 10 col/100 mL in both time periods.]**	
1985-1994 (Mott, 1997)	**1995-2011**
Mill Creek – T04: 14	Beech Creek** – T01: 13.0
Richland Creek* – T09: 14	Cecil Creek** – T03: 10.5
Calf Creek – T10: 11	Mill Creek – T04: 17.7
Bear Creek – T12*: 14	Davis Creek** – T07: 13.6
Tomahawk Creek – T14: 39	Calf Creek - T10: 12.3
Clabber Creek – T17: 15	Tomahawk Creek – T14: 39.7
*1995-2011, less than 10	Clabber Creek – T17: 15.0
**1985-1994, less than 10	Big Creek-Lower** – T18: 10.8



	T01	T02	T03	T04	T05	T06	T07	T08	T09	T10	T11	T12	T13	T14	T15	T16	T17	T18	T23	T24
🟦 Mean	31.9	39.8	39.9	43.4	40.6	20.4	43.6	54.1	26.5	128.0	18.5	24.4	27.5	86.2	16.6	19.3	74.7	27.1	20.0	32.5
🟥 Geomean	13.0	6.7	10.5	17.7	8.7	4.6	13.6	8.9	5.0	12.3	6.9	9.2	9.0	39.7	3.8	7.0	13.4	10.8	5.8	7.9
# of Samples	28	60	61	62	61	62	64	57	47	57	61	57	48	60	62	66	64	54	55	55

Figure 4.2.6 Geometric mean (geomean) and mean fecal coliform bacteria concentrations for Buffalo River tributary sites sampled between 1995-2011 during base-flow conditions.

Fecal coliform bacteria concentrations at Buffalo River corridor sites from 1999 through 2011 generally were similar but concentrations were substantially higher at T14 (Tomahawk Creek) and T04 (Mill Creek). The median concentration at T14 is 43.50

colonies/100 mL, approximately four times higher than the mean of the median concentrations of the other 19 sites (11.7 col/100 mL) (Figure 4.2.7).

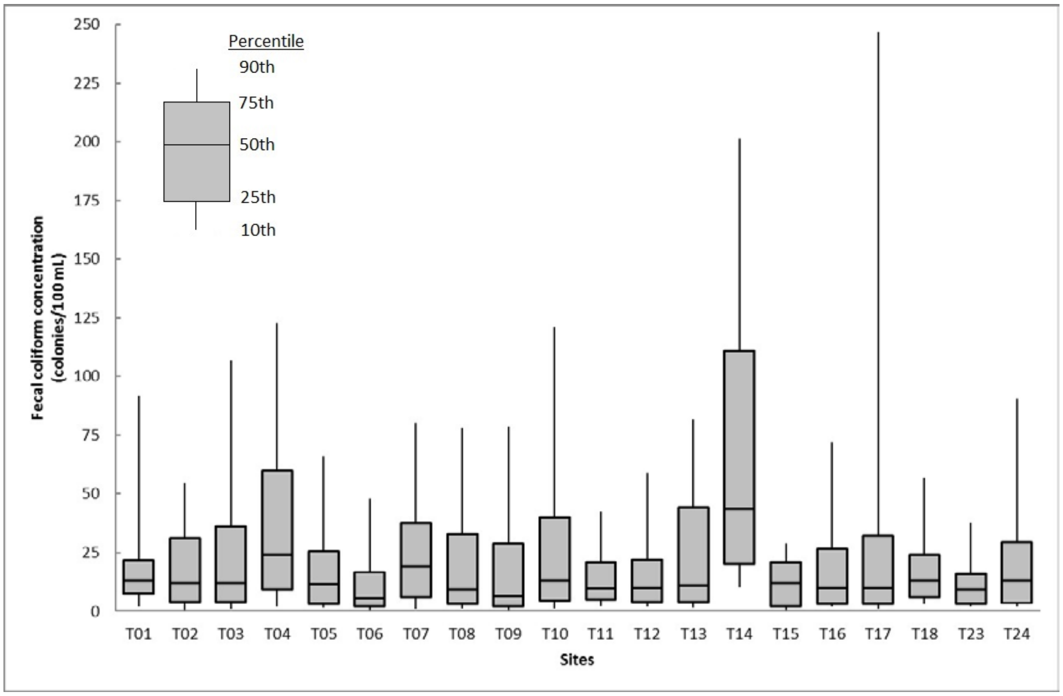
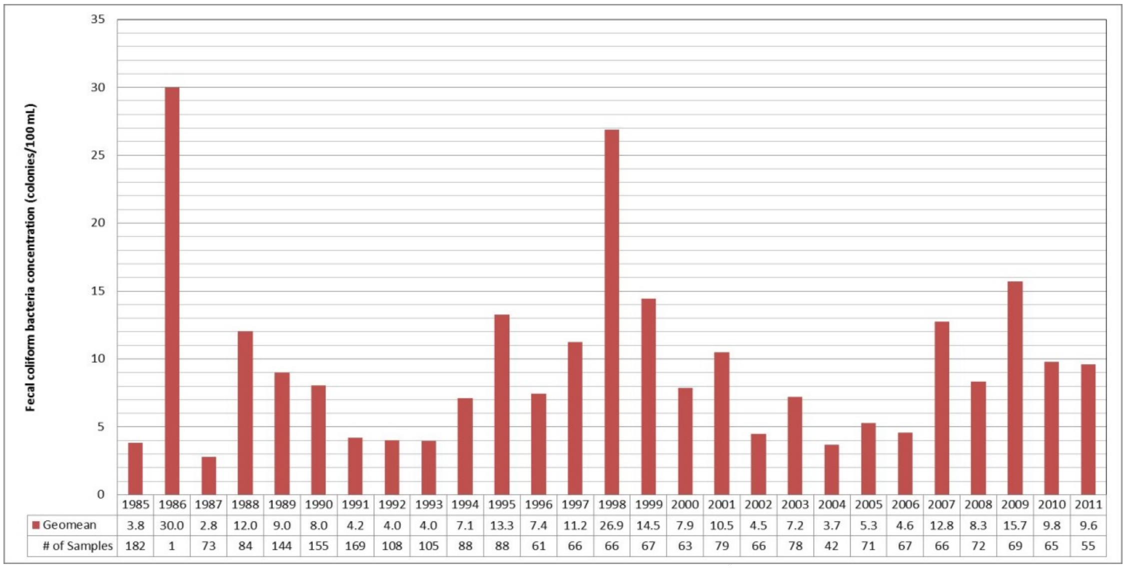


Figure 4.2.7 Fecal coliform bacteria concentrations for Buffalo River tributary sites sampled during base-flow conditions from 1999-2011.

The annual geometric means of fecal coliform bacteria concentrations for all of the tributaries from 1985-2011 generally did not exceed 10 col/100 mL (Figure 4.2.8). The highest geometric mean values occurred in 1986 and 1998, both 25 col/100 mL. From 1985– 1994 only one of these nine years had a geometric mean greater than 10 col/100 mL (11% of the time) with an overall mean geometric mean of 6.1 col/100 mL. Whereas, from 1995 – 2011, 7 of the 17 years were greater than 10 col/100 mL (41% of the time) with an overall average geometric mean of 10.2 col/100 mL; 1.7 times the average of the previous period.

Although base-flow data from 1995-2011 were insufficiently frequent to make an ultimate determination, it appears that the water quality standard for fecal coliform bacteria (geometric mean of 200 col/100 mL or a value for an individual sample of 400 col/100 mL) for primary contact seasons generally was being met. The water quality standard for fecal coliform bacteria for primary contact seasons is a geometric mean "calculated on a minimum of five (5) samples spaced evenly within a thirty (30)-day period" (Arkansas Pollution Control and Ecology Commission, 2015)." Therefore, the sampling frequency was insufficient for determining exceedance of the geometric mean standard. However, it is important to note that concentrations for only 33 tributary samples out of 1,141 collected during base-flow conditions between 1995-2011 were higher than 200 col/100 mL. Twelve of these 33 samples were collected at T17 (Water Creek, 7 samples) and T14 (Tomahawk Creek, 5 samples). The individual sample standard

(400 col/100 mL) was exceeded once or twice at T02 (Ponca Creek), T05 (Little Buffalo River), T07 (Big Creek), T08 (Cave Creek), T10 (Calf Creek), T14 (Tomahawk Creek), and T17 (Clabber Creek).



	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
■ Geomean	3.8	30.0	2.8	12.0	9.0	8.0	4.2	4.0	4.0	7.1	13.3	7.4	11.2	26.9	14.5	7.9	10.5	4.5	7.2	3.7	5.3	4.6	12.8	8.3	15.7	9.8	9.6
# of Samples	182	1	73	84	144	155	169	108	105	88	88	61	66	66	67	63	79	66	78	42	71	67	66	72	69	65	55

Figure 4.2.8 Annual geometric means for fecal coliform bacteria concentrations for Buffalo River tributary sites sampled from 1985-2011 during base-flow conditions.

Storm-Flow Conditions

Grab samples (9 to 18 per site) coinciding with storm-flow events on both the rising and falling limbs of the hydrograph were collected during storm-flow conditions. Higher fecal coliform bacteria concentrations are expected during storm-flow conditions, because surface-water runoff transports bacteria adsorbed to soil particles (Mott, 1990) and concentrations associated with these samples were often substantially higher than during base-flow conditions. However, variability of concentrations is very high and can be strongly affected by factors such as season, antecedent storm-flow events, rainfall duration and intensity, and position on the hydrograph (rising limb, falling limb, peak, etc.). Therefore, data from storm-flow events were not summarized.

Relation between Bacteria and Land Use

Correlation analysis (Spearman's rank correlation, which does not assume linearity of the relation or normality of the data) results indicate a correlation between pasture land use and fecal coliform bacteria concentrations in tributary watersheds (Figure 4.2.9). The fecal coliform data points represent the geometric mean of all samples collected during both base-flow and storm-flow conditions for each tributary from 1985-2011. A general upward trend is noted between increases in percent pasture within the tributary watershed area and increases in fecal coliform concentrations with a rho value of 0.58. The percent pasture for Mill Creek (T04) (16.7 percent) likely is underestimated because of the interbasin transfer from the Crooked Creek watershed (Mott and others, 2000) and a more accurate value for percent pasture would likely increase the rho value.

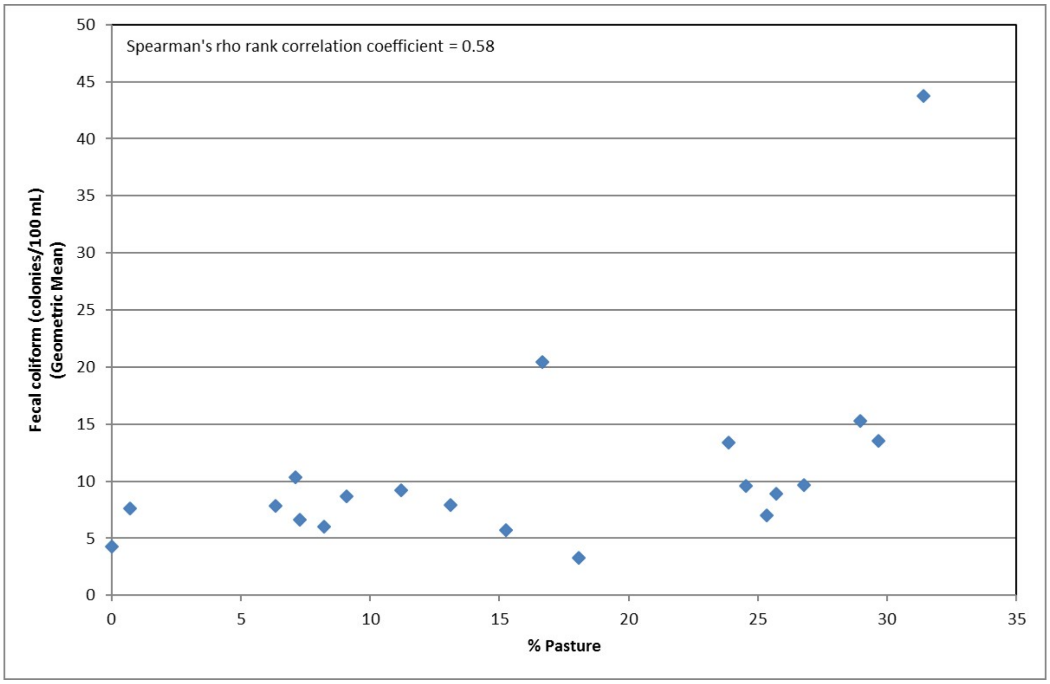


Figure 4.2.9 Relation between geometric mean fecal coliform bacteria concentrations and percent pasture of watersheds of Buffalo River tributary sites sampled between 1985-2011 during storm- flow and base-flow conditions.

4.3 Nitrate

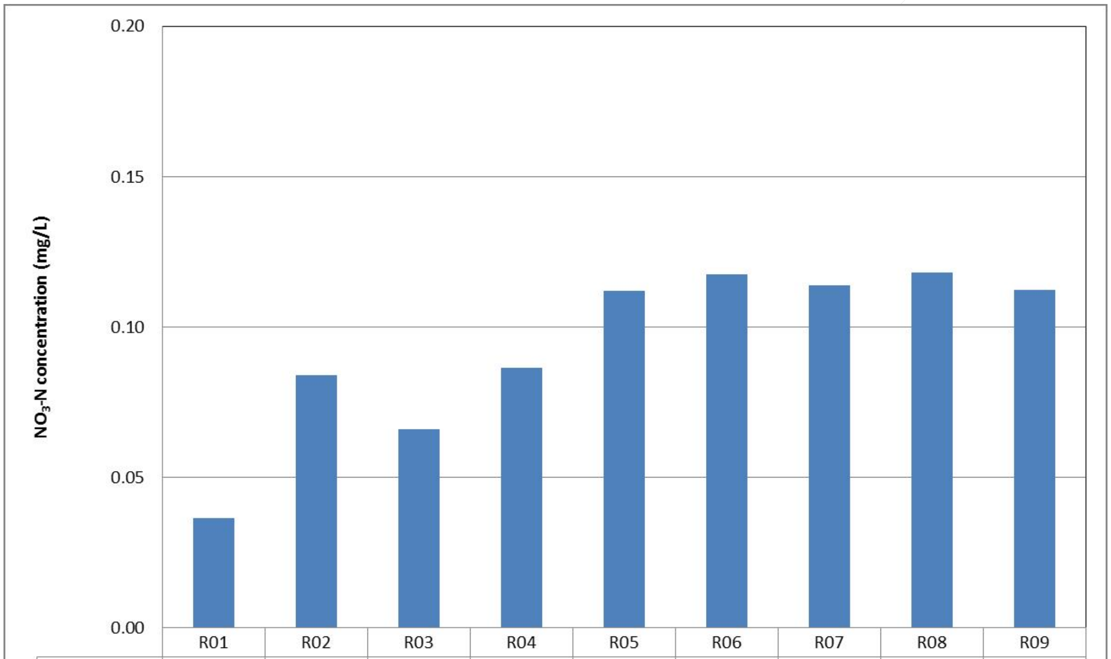
This section presents the data for samples analyzed for nitrate as nitrogen (NO_3-N). Samples were collected at the river corridor and tributary sites during base-flow and storm-flow conditions and the results are presented separately. For data where the concentration was less than the detection limit, a value of one half of the detection limit was used in the statistical analyses.

Surface-derived nitrate can enter streams during base-flow and storm-flow conditions. Sources of anthropogenic nitrate include animal manures, septic systems, and wastewater treatment systems. Manure from cattle operations and land-applied manure from confined animal operations generally enter streams during storm events, when storm water comes in contact with animal waste before it flows into the stream. If animals have regular access to streams then manure and urine can also enter the stream system during base-flow conditions, and a large part of the load in the stream can be contributed by groundwater. Wastewater discharges are generally constant and their effects are mostly seen during base-flow and low-flow conditions, when dilution resulting from storm-water runoff is largely absent. However, overflows from poor infrastructure can occur during storm events, which could result in higher discharges of contaminants associated with these older systems.

4.3.1 Buffalo River Corridor Sites

Base-Flow Conditions

The arithmetic means of NO_3-N concentrations were calculated for each river corridor site for the sampling period of 1995-2011 for samples collected during base-flow conditions (Figure 4.3.1). The number of samples collected at each site for this period ranged from 48 to 53. R01 (Wilderness Boundary) had the lowest concentrations with a mean concentration of 0.04 mg/L. All of the mean concentrations for the other river corridor sites ranged from 0.07 to 0.12 mg/L (at R08, Rush). With the exception of R01, mean concentrations for all of the sites were approximately 25% to 55% higher than mean nitrate concentrations for data collected from 1985-1994 (Mott, 1997).



	R01	R02	R03	R04	R05	R06	R07	R08	R09
■ Mean	0.04	0.08	0.07	0.09	0.11	0.12	0.11	0.12	0.11
# of Samples	48	51	52	52	51	53	52	51	51

Figure 4.3.1 Mean NO_3-N concentration for Buffalo River corridor sites sampled between 1995-2011 during base-flow conditions.

Examination of the distribution of base-flow conditions data at corridor sites indicated that NO_3-N concentrations generally increased in a downstream direction and were highest in the middle section of the Buffalo River (sites R05-R08) (Figure 4.3.2). Mott and Luraas (2004) also analyzed data for the years 1991-1998 using box plots. The trend found in Figure 4.3.2 in which the median NO_3-N concentration at R02 (Ponca) is higher than R01 (Wilderness Boundary) and R03 (Pruitt) (R01 being the most upstream Buffalo River site location) was also reported by Mott and Luraas (2004). In both study periods, the median concentrations were below 0.1 mg/L for all of the sites.

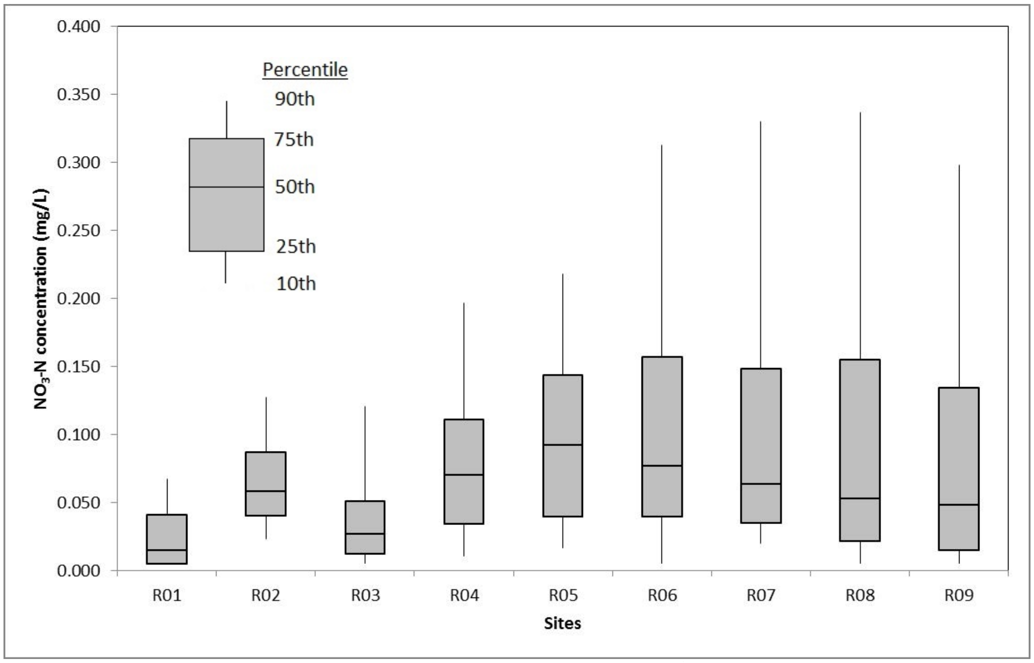
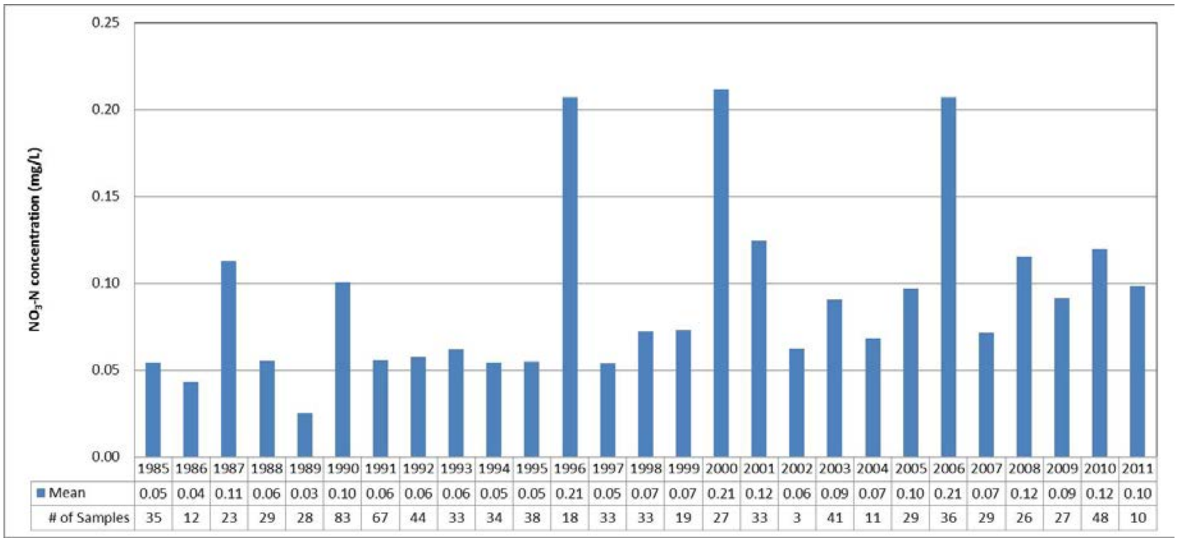


Figure 4.3.2 NO_3-N concentration for Buffalo River corridor sites sampled from 1999-2011 during base-flow conditions.



	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
■ Mean	0.05	0.04	0.11	0.06	0.03	0.10	0.06	0.06	0.06	0.05	0.05	0.21	0.05	0.07	0.07	0.21	0.12	0.06	0.09	0.07	0.10	0.21	0.07	0.12	0.09	0.12	0.10
# of Samples	35	12	23	29	28	83	67	44	33	34	38	18	33	33	19	27	33	3	41	11	29	36	29	26	27	48	10

Figure 4.3.3 Mean annual NO_3-N concentrations for Buffalo River corridor sites sampled from 1985-2011 during base-flow conditions.

Mean NO_3-N concentrations of base flow, river corridor samples generally increased with time between 1985-2011 (Figure 4.3.3). Mean concentrations ranged from 0.03 to 0.21 mg/L with the highest values occurring in 1996, 2000, and 2006.

Storm-Flow Conditions

Grab samples (10 to 17 per site) coinciding with storm-flow events on both the rising and falling limbs of the hydrograph were collected during storm-flow conditions. Higher nitrate concentrations are expected during storm-flow conditions and concentrations associated with these samples were often substantially higher than during base-flow conditions; concentrations can also be lowered if streamflow dominated by groundwater with higher nitrate concentrations is diluted by runoff with lower nitrate concentrations. However, variability of concentrations is very high and can be strongly affected by factors such as season, antecedent storm-flow events, rainfall duration and intensity, and position on the hydrograph (rising limb, falling limb, peak, etc.). Therefore, data from storm-flow events were not summarized.

Relation between Nitrate and Land Use

NO_3-N concentrations generally increased with increases in percent pasture area of the watershed area upstream of the sampling site with a Spearman's rho value of 0.73 (Figure 4.3.4). The NO_3-N data represent the arithmetic mean of all samples collected (base-flow and storm-flow) for each river corridor site.

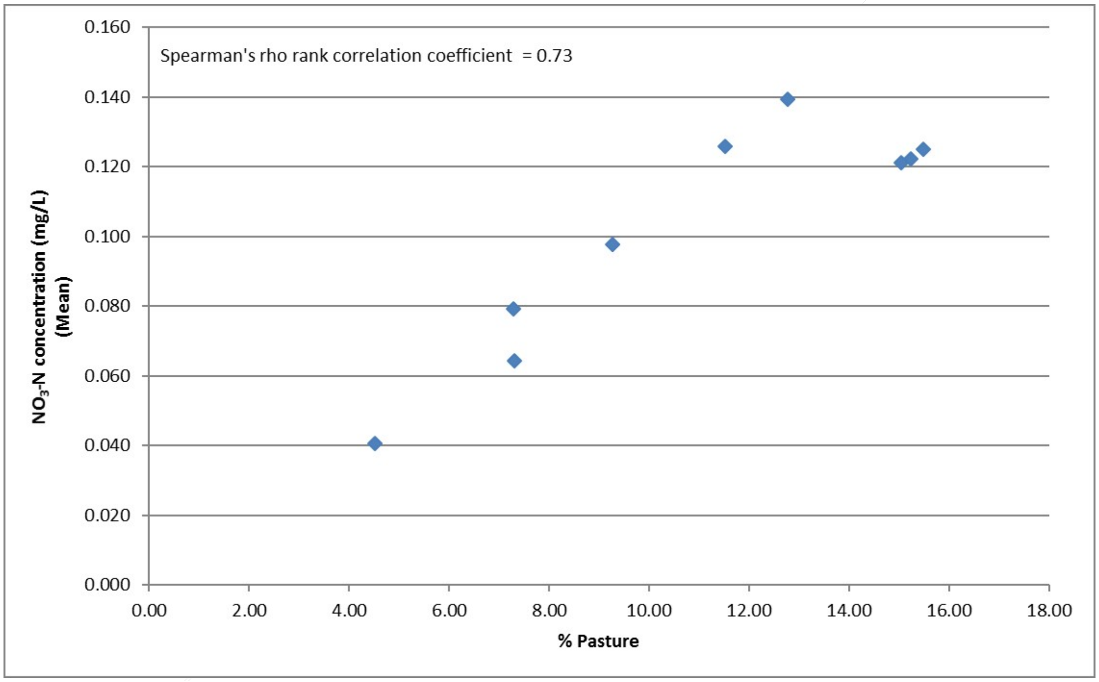


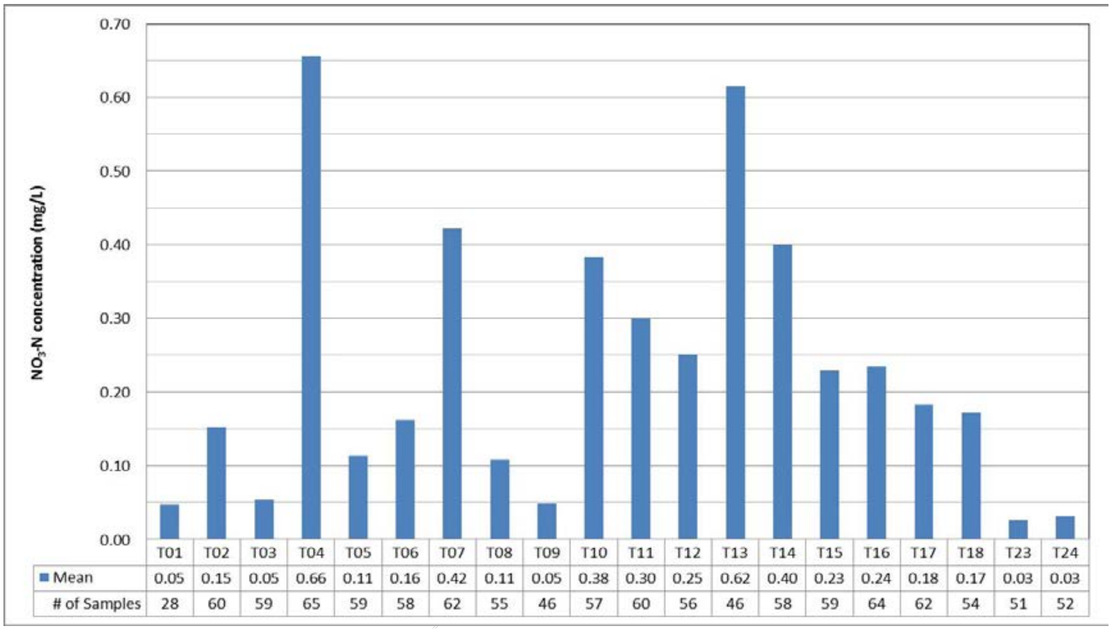
Figure 4.3.4 Relation between mean NO_3-N concentration and percent pasture of watersheds of Buffalo River corridor sites sampled between 1985-2011 during storm-flow and base-flow conditions for Buffalo River corridor

4.3.2 Buffalo River Tributary Sampling Sites

Base-Flow Conditions

The arithmetic mean NO_3-N concentrations among the tributary sites during base-flow conditions for the sampling period of 1995-2011 were quite variable and generally higher in tributaries in the middle part of the Buffalo River (sites T07-T14) (Figure 4.3.5). The number of samples collected at each site through this time-period ranged from 28 to 65. The mean NO_3-N concentrations ranged from 0.03 to 0.66 mg/L, with T04 (Mill Creek) and

T13 (Brush Creek) having the highest concentrations--each of which were greater than 0.6 mg/L. Data reported by Mott (1997) from 1985-1995 showed similar results with T04 and T13 having the highest concentrations compared to the other sites, but with slightly lower concentrations between 0.4 and 0.5 mg/L. This study and Mott (1997) showed tributary sites T07 (Davis Creek), T10 (Calf Creek), T11 (Mill Creek-Middle), and T14 (Tomahawk Creek) to have the next highest mean concentrations after T04 and T13. The mean NO_3-N concentrations in Mott (1997) were greater than or equal to 0.2 mg/L and less than 0.3 mg/L, whereas in the present study, the mean concentrations for sites T07, T10, T11, and T14 have increased and ranged from 0.30 mg/L to 0.42 mg/L.



	T01	T02	T03	T04	T05	T06	T07	T08	T09	T10	T11	T12	T13	T14	T15	T16	T17	T18	T23	T24
■ Mean	0.05	0.15	0.05	0.66	0.11	0.16	0.42	0.11	0.05	0.38	0.30	0.25	0.62	0.40	0.23	0.24	0.18	0.17	0.03	0.03
# of Samples	28	60	59	65	59	58	62	55	46	57	60	56	46	58	59	64	62	54	51	52

Figure 4.3.5 Mean NO_3-N concentrations for Buffalo River tributary sites between 1995-2011 during base-flow conditions.

Examination of the distribution of base-flow conditions data at tributary sites indicated that NO_3-N concentrations generally were lowest in tributaries in the upstream and downstream parts of the watershed and were highest in tributaries in the middle part of the watershed (Figure 4.3.6). Mott and Luraas (2004) analyzed data for the years 1991-1998 using box plots. The results shown in Figure 4.3.6 were similar to Mott and Luraas (2004) in that the median NO_3-N values for T04, T07, T10, T11 T13, and T14 were all above 0.2 mg/L. However, for this study concentrations for T12 and T15 also were above 0.2 mg/L and the median concentrations at T04 and T13 were both above 0.6 mg/L, whereas concentrations were between 0.4 and 0.6 mg/L for the Mott and Luraas (2004) evaluation period.

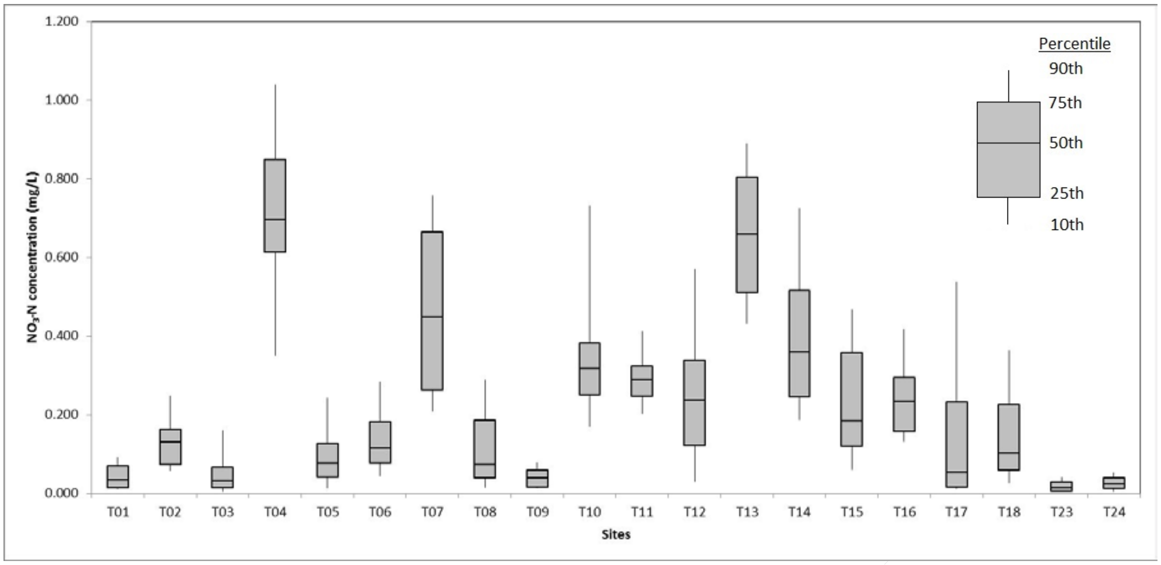
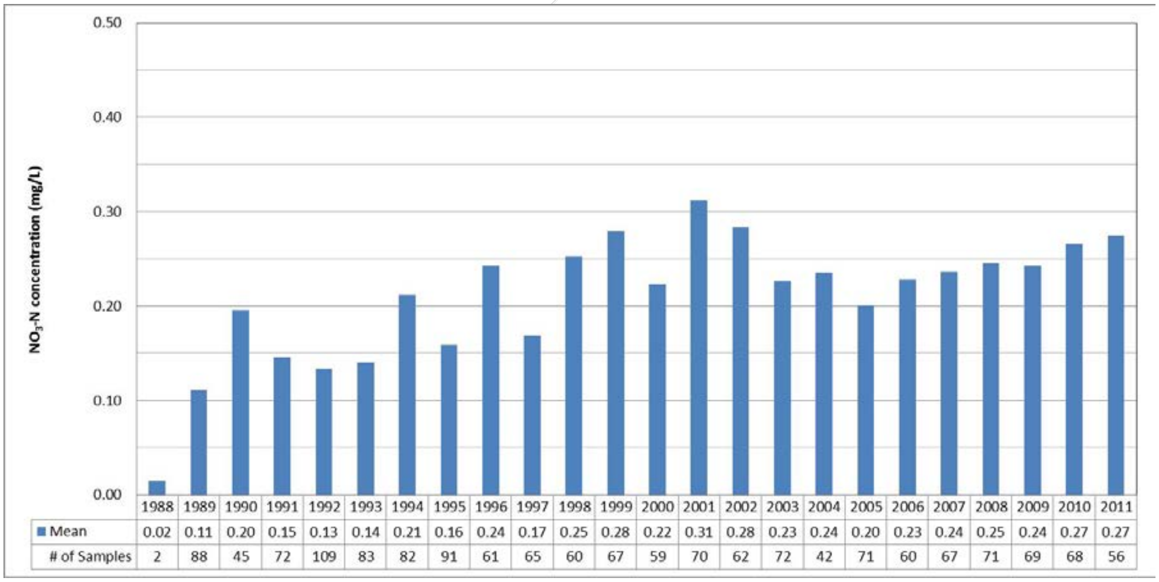


Figure 4.3.6 NO_3-N concentrations for Buffalo River tributary sites sampled from 1999-2011 during base-flow conditions

The arithmetic mean of base flow NO_3-N concentrations of all tributary samples generally increased between 1988 and 2011 (Figure 4.3.7). Mean concentrations ranged from 0.02 to 0.31 mg/L with the highest value occurring in 2001. Prior to 1998, the mean concentrations were less than 0.2 mg/L except for 1994 and 1996, when they were 0.21 mg/L and 0.24 mg/L, respectively. Beginning with 1998, mean concentrations were equal to or greater than 0.20 mg/L.



	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
■ Mean	0.02	0.11	0.20	0.15	0.13	0.14	0.21	0.16	0.24	0.17	0.25	0.28	0.22	0.31	0.28	0.23	0.24	0.20	0.23	0.24	0.25	0.24	0.27	0.27
# of Samples	2	88	45	72	109	83	82	91	61	65	60	67	59	70	62	72	42	71	60	67	71	69	68	56

Figure 4.3.7 Annual mean NO_3-N concentrations for Buffalo River tributary sites sampled from 1988-2011 during base-flow conditions.

Storm-Flow Conditions

Grab samples (3 to 13 per site) coinciding with storm-flow events on both the rising and falling limbs of the hydrograph were collected during storm-flow conditions. Higher nitrate concentrations are expected during storm-flow conditions and concentrations associated with these samples were often substantially higher than during base-flow conditions; concentrations can also be lowered if streamflow dominated by groundwater with higher nitrate concentrations is diluted by runoff with lower nitrate concentrations. However, variability of concentrations is very high and can be strongly affected by factors such as season, antecedent storm-flow events, rainfall duration and intensity, and position on the hydrograph (rising limb, falling limb, peak, etc.). Therefore, data from storm-flow events were not summarized.

Relation between Nitrate and Land Use

As at the corridor sites, NO_3-N concentrations at tributary sites generally increased with increases in percent pasture area of the watershed area upstream of the sampling site with a Spearman's rho value of 0.83 (Figure 4.3.8). The NO_3-N data represent the arithmetic mean of all samples collected (base-flow and storm-flow) for each river corridor site. The percent pasture for Mill Creek (T04, 16.7 percent) likely is underestimated because of the interbasin transfer from the Crooked Creek watershed and a more accurate value for percent pasture would likely increase the rho value.

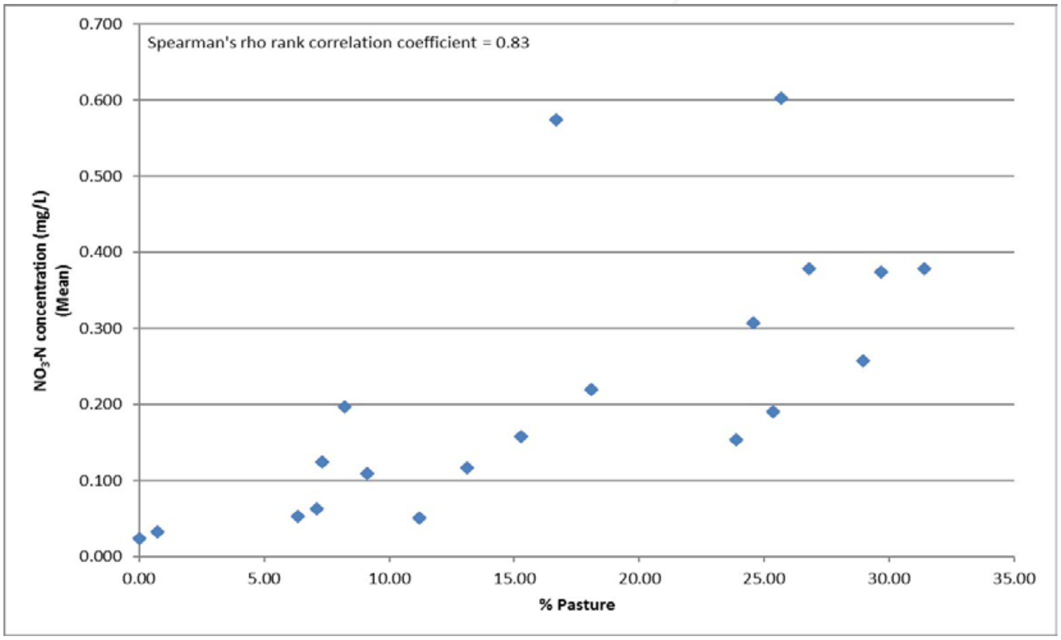


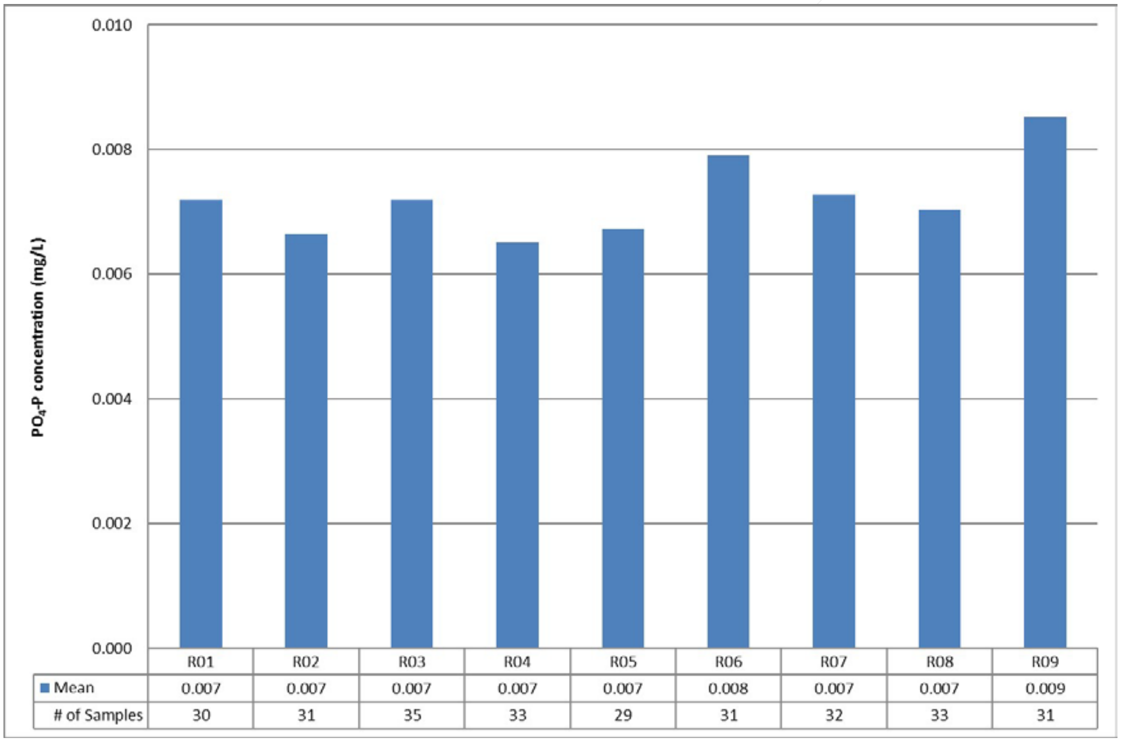
Figure 4.3.8 Relation between mean NO_3-N concentration and percent pasture for Buffalo River tributary sites sampled between 1985-2011 during storm-flow and base-flow conditions.

4.4 Orthophosphate

This section presents the data for samples analyzed for orthophosphate as phosphorus (PO_4-P). Base-flow data are presented for both the river corridor and tributary sites for the time period of 1998–2011. From 1998-2011 two detection limits (<0.005 and <0.01 mg/L) were used by the ADEQ laboratory (Jeff Ruehr, Arkansas Department of Environmental Quality, personal communication, March 2015). Values less than 0.010 mg/L (the highest detection limit) and values of <0.005 and <0.010 mg/L were set to 0.005 mg/L (one half of the highest detection limit) for use in the data analysis.

Instrumentation was changed at the ADEQ laboratory in September 2003 (Jeff Ruehr, Arkansas Department of Environmental Quality, personal communications, March 2015 and January 2017). Values greater than 0.005 mg/L, and even 0.01 mg/L, began to be reported more frequently immediately after this change in instrumentation. Therefore, laboratory instrumentation change presumably explains much of the difference between mean annual concentrations in 1998-2003 and 2004-2011.

Arithmetic mean PO_4-P concentrations for river corridor sites for base-flow samples for the period 1998-2011 were very similar, but tended to be slightly higher in the downstream part of the river (Figure 4.4.1). The mean concentrations ranged from 0.007 mg/L to 0.009 mg/L with the highest value at R09 (Mouth). The number of samples collected at each site for this time-period ranged from 29 to 33.

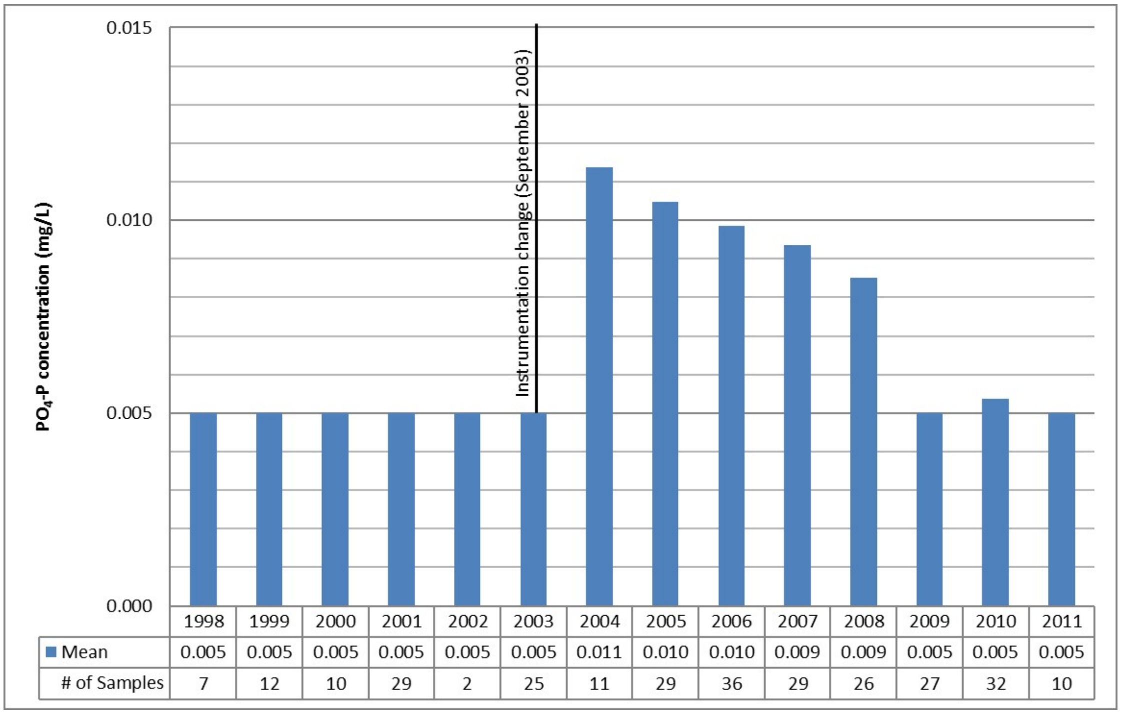


	R01	R02	R03	R04	R05	R06	R07	R08	R09
■ Mean	0.007	0.007	0.007	0.007	0.007	0.008	0.007	0.007	0.009
# of Samples	30	31	35	33	29	31	32	33	31

Figure 4.4.1 Mean PO_4-P concentrations for Buffalo River corridor sites sampled from 1998-2011 during base-flow conditions.

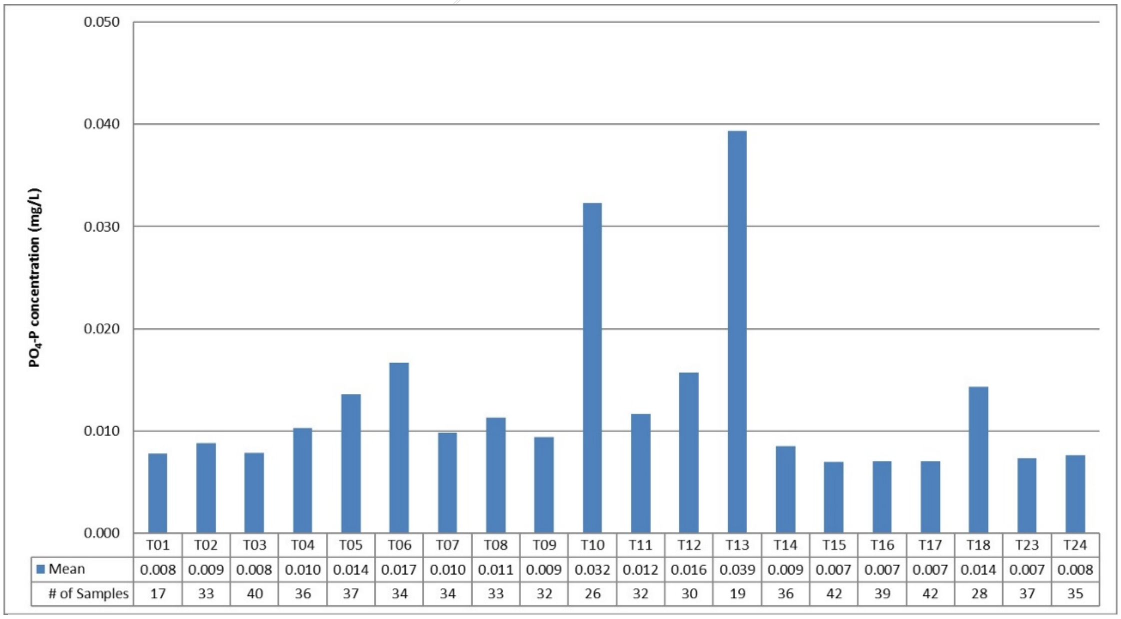
The mean PO_4-P concentrations of all base-flow river corridor samples were determined for each year beginning in 1998 and ending in 2011 (Figure 4.4.2). All of the mean concentrations were less than 0.012 mg/L. Mean concentrations from 1998-2003 uniformly were 0.005 mg/L and then increased substantially in 2004, presumably because of the laboratory instrumentation change. Mean concentrations generally decreased slightly from 2004-2011.

Mean PO₄-P concentrations were calculated for each tributary site for the sampling period of 1998 through 2011 for samples collected during base-flow conditions (Figure 4.4.3). The mean PO₄-P concentrations ranged from 0.007 to 0.039 mg/L with T10 (Calf Creek) and T13 (Brush Creek) having the highest values, with each greater than 0.03 mg/L. The number of samples collected at each site over this time period ranged from 17 to 42.



	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
■ Mean	0.005	0.005	0.005	0.005	0.005	0.005	0.011	0.010	0.010	0.009	0.009	0.005	0.005	0.005
# of Samples	7	12	10	29	2	25	11	29	36	29	26	27	32	10

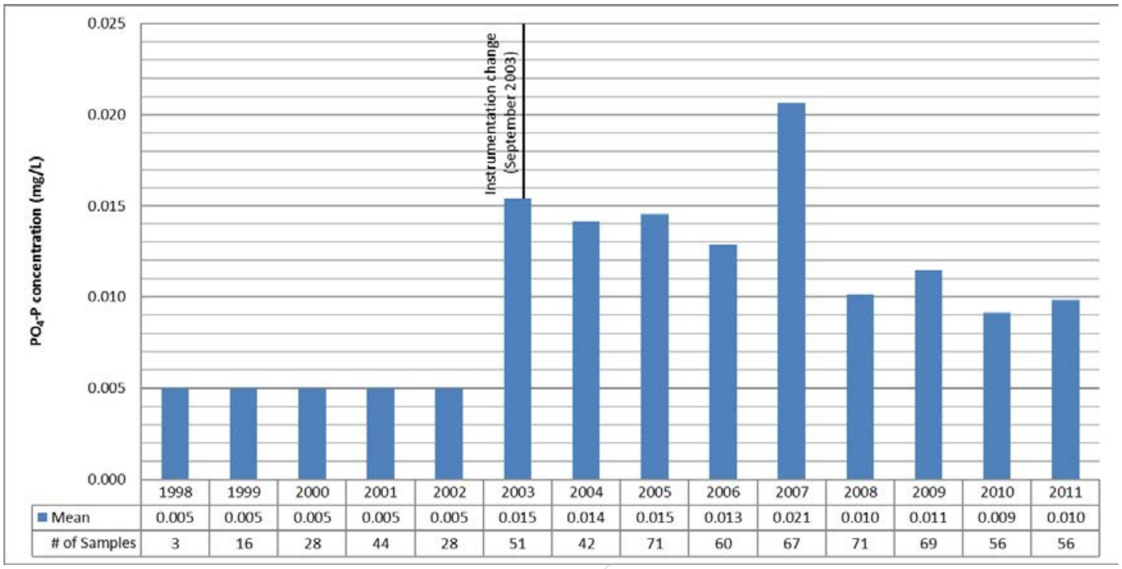
Figure 4.4.2 Annual mean PO$_4$-P concentration for Buffalo River corridor sites from 1998-2011 during base-flow conditions.



	T01	T02	T03	T04	T05	T06	T07	T08	T09	T10	T11	T12	T13	T14	T15	T16	T17	T18	T23	T24
■ Mean	0.008	0.009	0.008	0.010	0.014	0.017	0.010	0.011	0.009	0.032	0.012	0.016	0.039	0.009	0.007	0.007	0.007	0.014	0.007	0.008
# of Samples	17	33	40	36	37	34	34	33	32	26	32	30	19	36	42	39	42	28	37	35

Figure 4.4.3 Mean PO$_4$-P concentrations for Buffalo River tributary sites sampled from 1998-2011 during base-flow conditions.

The mean PO_4-P concentrations of all base-flow tributary samples were determined for each year beginning in 1998 and ending in 2011 (Figure 4.4.4). Mean values ranged from 0.005 to 0.021 mg/L with the highest value occurring in 2007. Mean concentrations from 1998-2002 uniformly were 0.005 mg/L and then increased substantially in 2003, presumably because of the laboratory instrumentation change. Mean concentrations generally decreased slightly from 2003-2011.

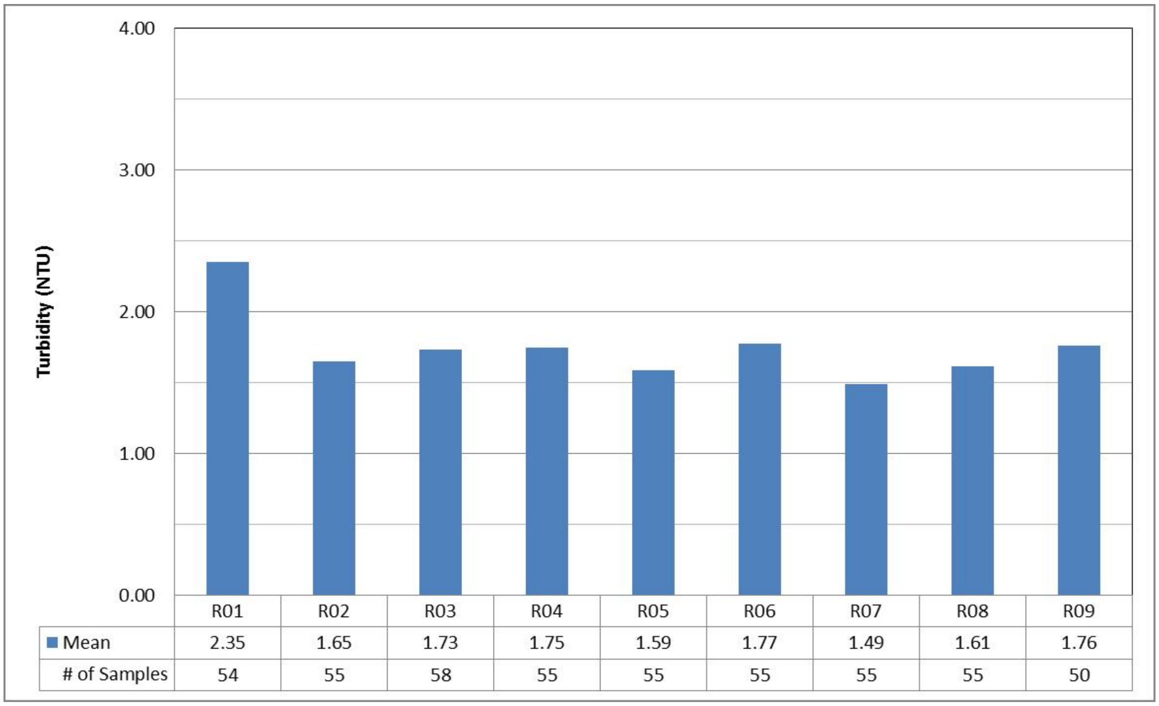


	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
■ Mean	0.005	0.005	0.005	0.005	0.005	0.015	0.014	0.015	0.013	0.021	0.010	0.011	0.009	0.010
# of Samples	3	16	28	44	28	51	42	71	60	67	71	69	56	56

Figure 4.4.4 Annual mean PO_4-P concentration for Buffalo River tributary sites sampled from 1998-2011 during base-flow conditions.

4.5 Turbidity

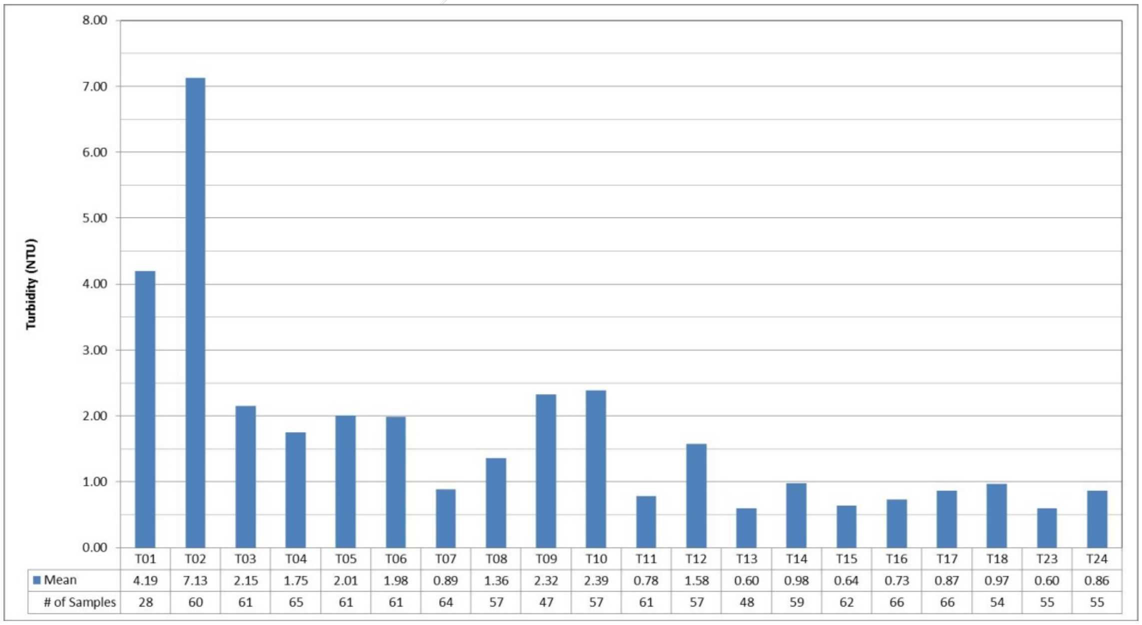
The arithmetic means of turbidity values for river corridor sites for the sampling period of 1995-2011 for samples collected during base-flow conditions varied little, ranging from 1.49 to 2.35 nephelometric turbidity units (NTU) (Figure 4.5.1). Mott (1997) attributed the higher values at R01 (Wilderness Boundary) as compared to the other sites to the geology of the area upstream from Boxley Valley. The watershed above R01 is dominated by interbedded Pennsylvanian aged sandstones and shales which contribute sediment in the form of clays weathered from the shale formations. Because of the differences in geology and resulting hydrology in the two areas (Kresse and others, 2014) groundwater (which would generally have low turbidity) contribution probably is also greater in the Boxley Valley area than upstream from R01. The number of measurements at each site over this time period ranged from 50 to 58.



	R01	R02	R03	R04	R05	R06	R07	R08	R09
■ Mean	2.35	1.65	1.73	1.75	1.59	1.77	1.49	1.61	1.76
# of Samples	54	55	58	55	55	55	55	55	50

Figure 4.5.1 Mean turbidity values for Buffalo River corridor sites sampled between 1995-2011 during base-flow conditions.

Arithmetic mean turbidity values for tributary sites for the period of 1995-2011 for values measured during base-flow conditions generally were lower in the eastern part of the watershed (Figure 4.5.2). In general, there is less underlying sandstone and shale in watersheds contributing to the upstream part of the Buffalo River watershed (Figure 2.1.1). With the exception of T01 (Beech Creek) and T02 (Ponca Creek), the mean turbidity values for the tributary sites were less than 2.40 NTU. T01 and T02 were 4.19 and 7.13 NTU, respectively. The mean turbidity for T01 was similar to the value listed in Mott (1997), whereas for T02, the 1995-



	T01	T02	T03	T04	T05	T06	T07	T08	T09	T10	T11	T12	T13	T14	T15	T16	T17	T18	T23	T24
■ Mean	4.19	7.13	2.15	1.75	2.01	1.98	0.89	1.36	2.32	2.39	0.78	1.58	0.60	0.98	0.64	0.73	0.87	0.97	0.60	0.86
# of Samples	28	60	61	65	61	61	64	57	47	57	61	57	48	59	62	66	66	54	55	55

Figure 4.5.2 Mean turbidity for Buffalo River tributary sites sampled between 1995-2011 during base-flow conditions.

2011 value was greater than three times the mean value from 1985-1994 (Mott, 1997). The number of samples collected at each site for this time period ranged from 28 to 66.

4.6 Dissolved Oxygen, Water Temperature, and pH

This section presents the results of *in situ* measurements of dissolved oxygen, water temperature, and pH at the river corridor and tributary sites during base-flow conditions. The *in situ* data for dissolved oxygen, water temperature, and pH were plotted for both the river corridor and tributary sites and compared to water quality standards. These plots can be found in Appendix 2; means and standard deviations are tabulated in Appendix 3. A summary of the statistical analyses of this data is presented in the following sections for both river corridor and tributary sites.

4.6.1 Buffalo River Corridor Sites

Dissolved oxygen concentrations at each river corridor site for a sampling period of 1995-2011 during base-flow conditions seldom were below the standard for minimum dissolved oxygen concentration (6 mg/L at all sites and all water temperatures; Table 4.6.1). Dissolved oxygen concentrations ranged from 3.5 mg/L at R01 (Wilderness Boundary) to 18.5 mg/L at R07 (Highway 14) for river corridor sites. When concentrations were compared to the standard for dissolved oxygen, only four samples fell below the minimum during the monitoring period with two occurring at site R01 and two at site R02 (Ponca).

Parameter: Dissolved Oxygen Standard: 6 mg/L						
Site	**Minimum**	**Maximum**	**Mean**	**Geometric Mean**	**Ecoregion**	**# Below Standard**
R01	3.5	15.0	9.5	9.2	BM	2
R02	5.4	15.3	9.9	9.6	BM	2
R03	6.8	14.5	10.0	9.7	BM	0
R04	6.5	14.2	9.8	9.6	BM	0
R05	6.6	15.5	10.2	10.0	BM	0
R06	6.7	16.3	10.7	10.4	OH	0
R07	6.5	18.5	10.6	10.4	OH	0
R08	6.6	17.5	10.1	9.9	OH	0
R09	6.8	16.2	10.2	10.0	OH	0
					Total	**4**

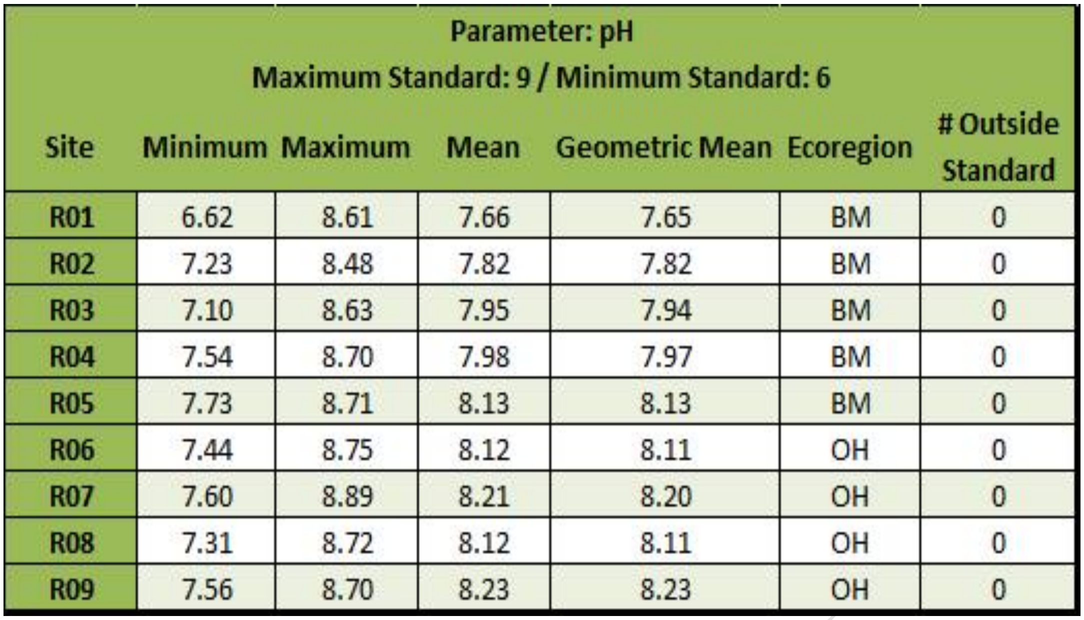
Table 4.6.1 Dissolved oxygen concentration statistics for Buffalo River corridor sites sampled between 1995-2011 during base-flow conditions.

Water temperature for river corridor sites in the Ozark Highlands for the sampling period of 1995-2011 during base-flow conditions often exceeded water quality standards for water temperature during June through August (Table 4.6.2). River corridor sites R01 (Wilderness Boundary) to R05 (Woolum) fall within the Boston Mountains (BM) and have a maximum temperature standard of 31°C. Meanwhile, corridor sites R06 (Gilbert) to R09 (Mouth) are located within the Ozark Highlands (OH) and have a maximum water temperature standard of 29°C. Water temperature measurements ranged from 0.2°C (R03, Pruitt) to 33.4°C (R08, Rush). Overall, 35 different measurements (of 493) exceeded the aforementioned standards and 32 of the 35 occurred within the Ozark Highlands. More than half of all measurements (31 of 60) made during June through August at river corridor sites in the Ozark Highlands exceeded the standard.

Parameter: Water Temperature BM Standard: 31°C / OH Standard: 29°C						
Site	**Minimum**	**Maximum**	**Mean**	**Geometric Mean**	**Ecoregion**	**# Exceeded Standard**
R01	1.8	25.1	14.7	12.4	BM	0
R02	0.8	28.1	15.5	12.8	BM	0
R03	0.2	30.5	17.4	13.4	BM	0
R04	0.3	30.5	17.8	14.5	BM	0
R05	1.1	32.0	18.9	15.9	BM	3
R06	2.3	31.8	18.6	16.0	OH	6
R07	2.1	33.1	17.8	14.7	OH	8
R08	1.6	33.4	17.6	14.7	OH	7
R09	3.2	32.9	18.4	16.0	OH	11
					Total	**35**

Table 4.6.2 Water temperature statistics for Buffalo River corridor sites sampled between 1995-2011 during base-flow conditions.

Values for all pH samples collected between 1999 and 2011 for river corridor sites during base-flow conditions were between 6 and 9 which is the allowable pH range as set by Regulation 2 (Table 4.6.3). The minimum recorded pH was 6.62 (R01, Wilderness Boundary) and the maximum was 8.89 (R07, Highway 14).



Parameter: pH
Maximum Standard: 9 / Minimum Standard: 6

Site	Minimum	Maximum	Mean	Geometric Mean	Ecoregion	# Outside Standard
R01	6.62	8.61	7.66	7.65	BM	0
R02	7.23	8.48	7.82	7.82	BM	0
R03	7.10	8.63	7.95	7.94	BM	0
R04	7.54	8.70	7.98	7.97	BM	0
R05	7.73	8.71	8.13	8.13	BM	0
R06	7.44	8.75	8.12	8.11	OH	0
R07	7.60	8.89	8.21	8.20	OH	0
R08	7.31	8.72	8.12	8.11	OH	0
R09	7.56	8.70	8.23	8.23	OH	0

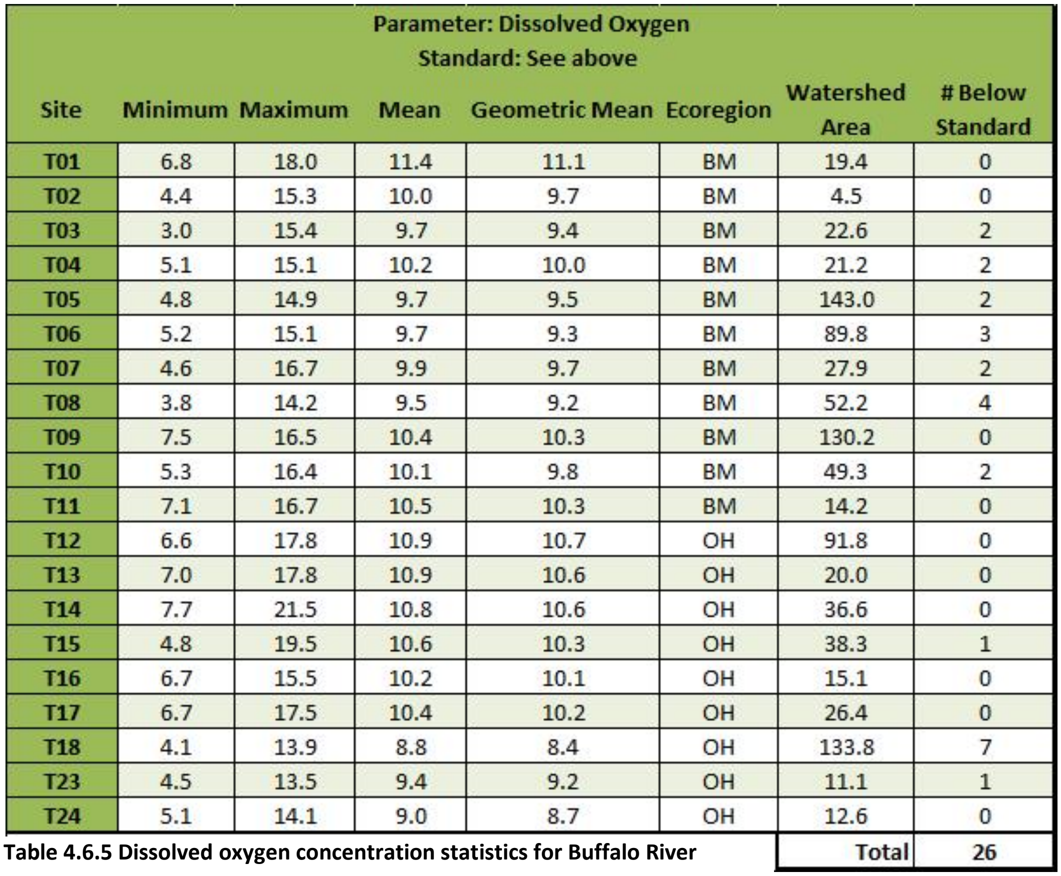
Table 4.6.3 pH statistics for Buffalo River corridor sites sampled between 1999-2011 during base-flow conditions.

4.6.2 Buffalo River Tributary Sites

The minimum state dissolved oxygen standards in Regulation 2 depend on ecoregion, watershed area, and water temperature. Table 4.6.4 details the criteria establishing standards for each tributary. Statistics for dissolved oxygen concentration for each tributary site during the sampling period of 1995-2011 at base-flow conditions are located in Table 4.6.5. Dissolved oxygen concentration ranged from 3.0 mg/L at T03 (Cecil Creek) to 21.5 mg/L at T14 (Tomahawk Creek) for tributary sites. When compared to the Regulation 2 dissolved oxygen concentration standard, 26 of 1,103 samples were below the minimum standard during the monitoring period. Most of these 26 values were from July, August, and September.

Ecoregion	Watershed Size	Primary Limit (mg/L)*	Critical Limit (mg/L)**
BM	>10 mi^2	6	6
BM	<10 mi^2	6	2
OH	>100 mi^2	6	6
OH	10-100 mi^2	6	5
OH	<10 mi^2	6	2

Table 4.6.4 Regulation 2 water quality standards for dissolved oxygen concentration
*** Primary refers to the period of the year when water temperatures are less than or equal to 22 degrees Celsius**
**** Critical refers to the period of the year when water temperatures exceed 22 degrees Celsius**



Site	Minimum	Maximum	Mean	Geometric Mean	Ecoregion	Watershed Area	# Below Standard
Parameter: Dissolved Oxygen Standard: See above							
T01	6.8	18.0	11.4	11.1	BM	19.4	0
T02	4.4	15.3	10.0	9.7	BM	4.5	0
T03	3.0	15.4	9.7	9.4	BM	22.6	2
T04	5.1	15.1	10.2	10.0	BM	21.2	2
T05	4.8	14.9	9.7	9.5	BM	143.0	2
T06	5.2	15.1	9.7	9.3	BM	89.8	3
T07	4.6	16.7	9.9	9.7	BM	27.9	2
T08	3.8	14.2	9.5	9.2	BM	52.2	4
T09	7.5	16.5	10.4	10.3	BM	130.2	0
T10	5.3	16.4	10.1	9.8	BM	49.3	2
T11	7.1	16.7	10.5	10.3	BM	14.2	0
T12	6.6	17.8	10.9	10.7	OH	91.8	0
T13	7.0	17.8	10.9	10.6	OH	20.0	0
T14	7.7	21.5	10.8	10.6	OH	36.6	0
T15	4.8	19.5	10.6	10.3	OH	38.3	1
T16	6.7	15.5	10.2	10.1	OH	15.1	0
T17	6.7	17.5	10.4	10.2	OH	26.4	0
T18	4.1	13.9	8.8	8.4	OH	133.8	7
T23	4.5	13.5	9.4	9.2	OH	11.1	1
T24	5.1	14.1	9.0	8.7	OH	12.6	0
						Total	26

Table 4.6.5 Dissolved oxygen concentration statistics for Buffalo River tributary sites sampled between 1995-2011 during base-flow conditions

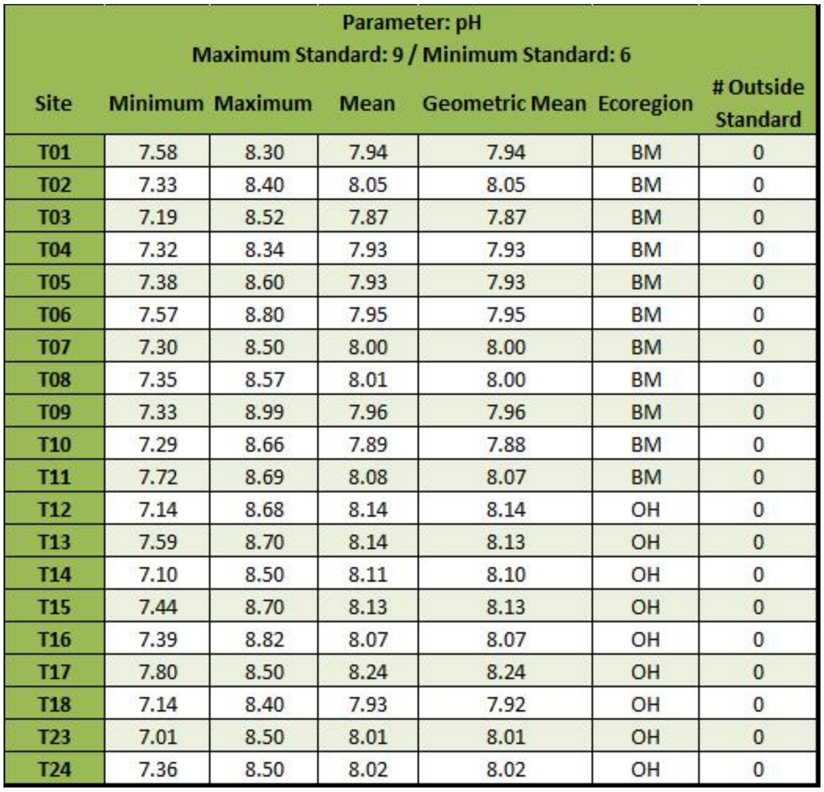
Water temperature for tributary sites during base-flow for the sampling period of 1995-2011 seldom exceeded the water quality standard (Table 4.6.6). Tributary sites T01 (Beech Creek) to T11 (Mill Creek-Middle) fall within the Boston Mountains and have a maximum temperature standard of 31°C. Meanwhile, tributary sites T12 (Bear Creek) to T24 (Leatherwood Creek) are located within the Ozark Highlands and have a maximum water temperature standard of 29°C. Water temperature measurements ranged from 0.4°C (T01, Beech Creek) to 32.3°C (T06, Big Creek). For tributary sites, only 9 of 1,135 measurements exceeded the water quality standard.

Parameter: Water Temperature
BM Standard: 31°C / OH Standard: 29°C

Site	Minimum	Maximum	Mean	Geometric Mean	Ecoregion	# Exceeded Standard
T01	0.4	22.8	9.6	7.6	BM	0
T02	1.4	24.3	13.5	11.5	BM	0
T03	3.5	28.6	14.7	13.1	BM	0
T04	3.6	26.4	15.5	14.0	BM	0
T05	1.0	30.8	16.6	13.8	BM	0
T06	4.6	32.3	17.8	16.0	BM	1
T07	3.8	25.4	15.3	14.3	BM	0
T08	4.0	30.3	17.4	15.5	BM	0
T09	5.4	30.3	15.6	14.4	BM	0
T10	4.8	26.0	16.8	15.8	BM	0
T11	4.5	23.0	15.0	14.2	BM	0
T12	2.6	30.9	16.8	14.4	OH	3
T13	1.9	23.7	14.2	12.4	OH	0
T14	4.8	29.8	16.0	14.7	OH	1
T15	3.2	27.2	15.2	13.3	OH	0
T16	6.3	22.4	14.5	13.7	OH	0
T17	1.8	31.2	15.5	13.1	OH	3
T18	4.3	30.7	16.4	14.4	OH	1
T23	4.2	25.6	14.8	13.5	OH	0
T24	2.9	27.3	15.9	14.3	OH	0
					Total	**9**

Table 4.6.6 Water temperature statistics for Buffalo River tributary sites sampled between 1995-2011 during base-flow conditions

Values for pH measured between 1999 and 2011 for river corridor sites during base-flow conditions were between 6 and 9 which is the allowable pH range as set by Regulation 2 (Table 4.6.7). The minimum recorded pH was 7.01 (T23, Middle Creek) and the maximum was 8.99 (T09, Richland Creek).



Site	Minimum	Maximum	Mean	Geometric Mean	Ecoregion	# Outside Standard
Parameter: pH Maximum Standard: 9 / Minimum Standard: 6						
T01	7.58	8.30	7.94	7.94	BM	0
T02	7.33	8.40	8.05	8.05	BM	0
T03	7.19	8.52	7.87	7.87	BM	0
T04	7.32	8.34	7.93	7.93	BM	0
T05	7.38	8.60	7.93	7.93	BM	0
T06	7.57	8.80	7.95	7.95	BM	0
T07	7.30	8.50	8.00	8.00	BM	0
T08	7.35	8.57	8.01	8.00	BM	0
T09	7.33	8.99	7.96	7.96	BM	0
T10	7.29	8.66	7.89	7.88	BM	0
T11	7.72	8.69	8.08	8.07	BM	0
T12	7.14	8.68	8.14	8.14	OH	0
T13	7.59	8.70	8.14	8.13	OH	0
T14	7.10	8.50	8.11	8.10	OH	0
T15	7.44	8.70	8.13	8.13	OH	0
T16	7.39	8.82	8.07	8.07	OH	0
T17	7.80	8.50	8.24	8.24	OH	0
T18	7.14	8.40	7.93	7.92	OH	0
T23	7.01	8.50	8.01	8.01	OH	0
T24	7.36	8.50	8.02	8.02	OH	0

Table 4.6.7 pH statistics for Buffalo River tributary sites sampled between 1999-2011 during base-flow conditions

4.7 Additional Parameters

Other parameters evaluated were specific conductance, sulfate, chloride, fluoride, and alkalinity. Graphical and statistical analysis of data for the river corridor and tributary sites are located in Appendix 2 and Appendix 3. Additional analyses of water temperature also are located in Appendix 2 and Appendix 3. Specific conductance and concentrations of alkalinity, sulfate, chloride, and fluoride at Buffalo River corridor sites generally increased in a downstream direction. Specific conductance and alkalinity increased because of the increasing influence of the carbonate geology in the Mississippian and Ordovician layers (Mott, 1997). Conductance and concentrations of sulfate, chloride, and alkalinity were substantially lower at site R01 (Wilderness Boundary) than at any other corridor site. Conductance and alkalinity at tributary sites also were influenced by geology.

4.8 Seasonal Patterns

Seasonal patterns were not investigated thoroughly because it was outside the scope of this report. However, it is likely that there are seasonal differences in water quality that are related to seasonal differences in streamflow and other factors. For example, specific conductance and concentrations of sulfate, chloride, and alkalinity and other dissolved ions likely decrease because of dilution during periods of higher streamflow. Other parameters such as nutrients and turbidity could be affected by either biological uptake of nutrients by algae or increased turbidity resulting from phytoplankton growth. A cursory examination (not shown) of nitrate, orthophosphate, and turbidity data did not reveal obvious seasonal patterns.

4.9 Springs

The locations of three springs sampled as part of the BNR monitoring program, S02 (Luallen Spring), S33 (Mitch Hill Spring), and S41 (Gilbert Spring) are shown in Figure 3.1.1. The springs are characterized by different geology and land use (Mott, 1997). Luallen Spring is in a relatively undisturbed area in the Boston Mountains. Mitch Hill Spring and Gilbert Spring are in the Springfield Plateau in areas of beef cattle operations. Mitch Hill Spring is affected by rural septic systems and Gilbert Spring is affected by urban land use (septic leachate from Gilbert, yard fertilizers) and some dairy operations. In general, springs in the Springfield Plateau are more susceptible to surface sources of contamination than springs in the Boston Mountains because of its karstic geology (Mott, 1997).

For the 1995-2011 sampling period, fecal coliform bacteria geometric means were highest at the springs in the Springfield Plateau (Gilbert Spring and Mitch Hill Spring). Comparing the 1985-1994 period (Mott, 1997) and the 1995-2011 period, geometric means decreased at Luallen Spring (from 4 to 2 colonies/100 mL) and at Gilbert Spring (from 11 to 8 colonies/100 mL) and increased at Mitch Hill Spring (from 3 to 5 colonies/100 mL). During both time periods, geometric means were highest at Gilbert Spring.

Examination of the distribution of data from 1999 through 2011 indicated that fecal coliform bacteria concentrations generally were greatest at Gilbert Spring (S41) (Figure 4.9.1). Median (50th percentile) fecal coliform bacteria concentrations from 1999 through 2011 were very similar for all three springs but were highest at Gilbert Spring and lowest at Luallen Spring (S02) (Figure 4.9.1). For each spring, the median concentration from 1999 through 2011 was similar to or slightly higher than the median for concentrations from 1991-1998 (Mott and Luraas, 2004).

Mean NO_3-N concentrations were lowest at Luallen Spring and substantially higher at Mitch Hill Spring and Gilbert Spring (the two springs in the Springfield Plateau) for the 1995-2011 monitoring period. When comparing data collected from 1985-1994 (Mott, 1997) to data from 1995-2011, means increased at Mitch Hill Spring (from 0.552 to 0.944 mg/L) and at Gilbert Spring (from 0.791 to 0.929 mg/L) and decreased at Luallen Spring (from 0.296 to 0.223 mg/L). Mean NO_3-N concentrations at all springs tended to be higher than concentrations from most surface water sites.

Examination of the distribution of data from 1999 through 2011 indicated that NO_3-N concentrations generally were greatest at Mitch Hill Spring (Figure 4.9.2). Median (50th percentile) NO_3-N concentrations from 1999 through 2011 at Mitch Hill Spring and Gilbert Spring were substantially higher than the median at Luallen Spring (Figure 4.9.2). Median concentrations at Luallen Spring and Gilbert Spring from 1991-1998 (Mott and Luraas, 2004) and 1999-2011 were similar. Median concentrations for Mitch Hill Spring from 1999-2011 were approximately double the values from the earlier monitoring period.

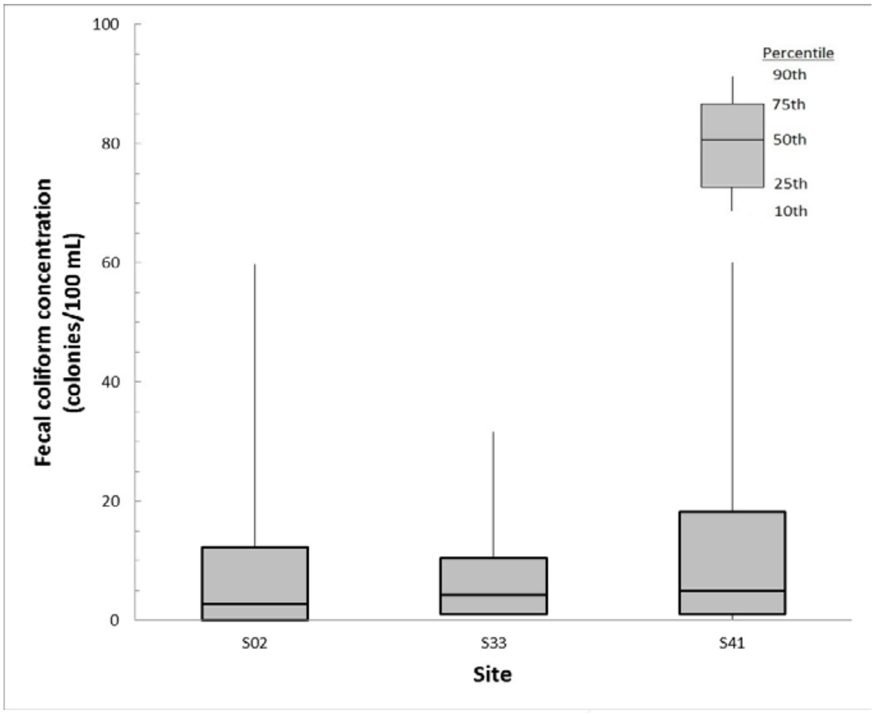


Figure 4.9.1 Fecal coliform bacteria concentrations for Buffalo River spring sites sampled during base-flow conditions from 1999-2011.

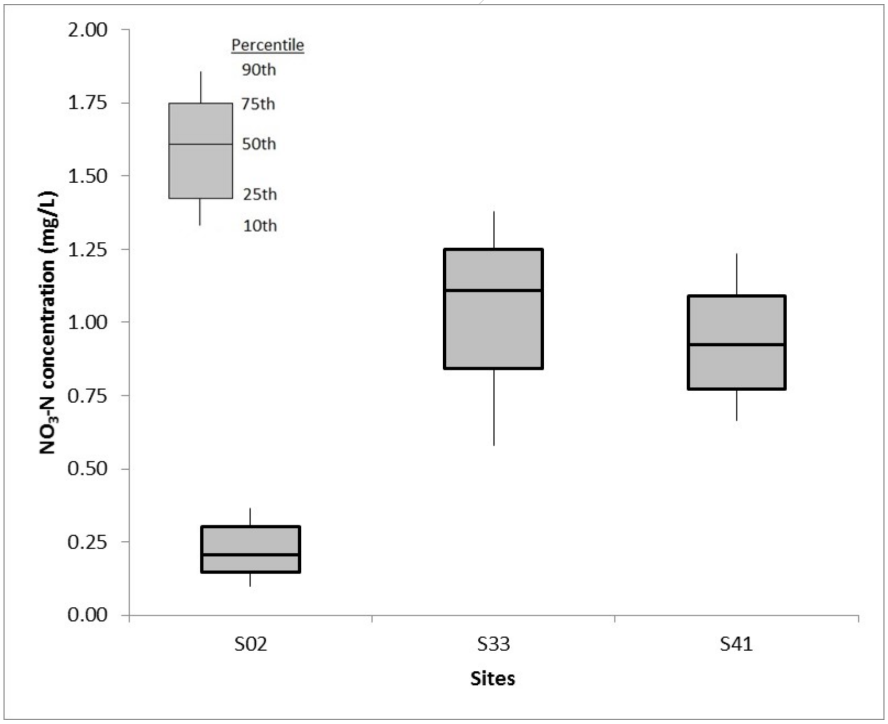


Figure 4.9.2 NO_3-N concentrations for Buffalo River spring sites sampled from 1999-2011 during base-flow conditions

Examination of the distribution of data from 2002 through 2011 indicated that PO_4-P concentrations generally were greatest at Gilbert Spring (Figure 4.9.3). Median (50th percentile) PO_4-P concentrations from 2003 through 2011 were highest at Gilbert Spring and lowest at Mitch Hill Spring (Figure 4.9.3).

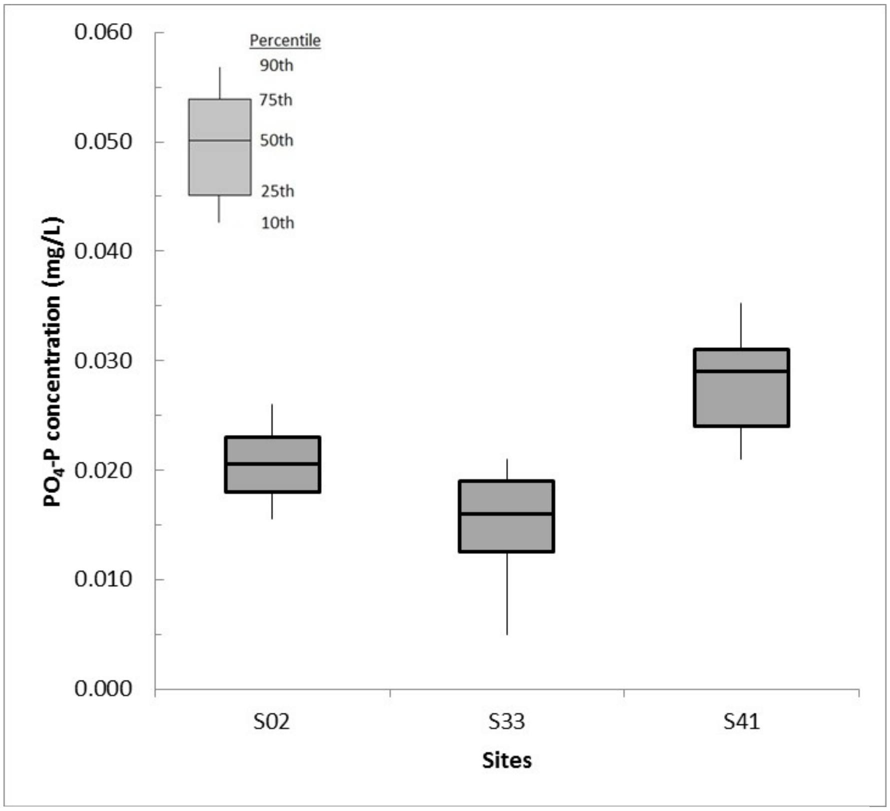


Figure 4.9.3 PO_4-P concentrations for Buffalo River spring sites sampled from 1999-2011 during base-flow conditions

Between the 1985-1994 period (Mott, 1997) and the 1995-2011 period, mean water temperature decreased substantially at the three springs (Figure 4.9.4). Means decreased at Luallen Spring (from 13.58 to 12.80°C), at Mitch Hill Spring (from 14.93 to 14.59°C), and at Gilbert Spring (from 15.14 to 14.41°C). During both time periods mean water temperatures were substantially lower at Luallen Spring than at the other two springs.

Between the 1985-1994 period (Mott, 1997) and the 1995-2011 period, mean specific conductance increased substantially at the three springs (Figure 4.9.5). Means increased at Luallen Spring (from 193.48 to 239.70 microsiemens per centimeter at 25°C), at Mitch Hill Spring (from 313.78 to 412.03 microsiemens per centimeter at 25°C), and at Gilbert Spring (from 318.33 to 397.26 microsiemens per centimeter at 25°C). During both time periods, means were substantially lower at Luallen Spring than at the other two springs. Mott (1997) attributes this difference to the lack of carbonate geology in the Luallen Spring area.

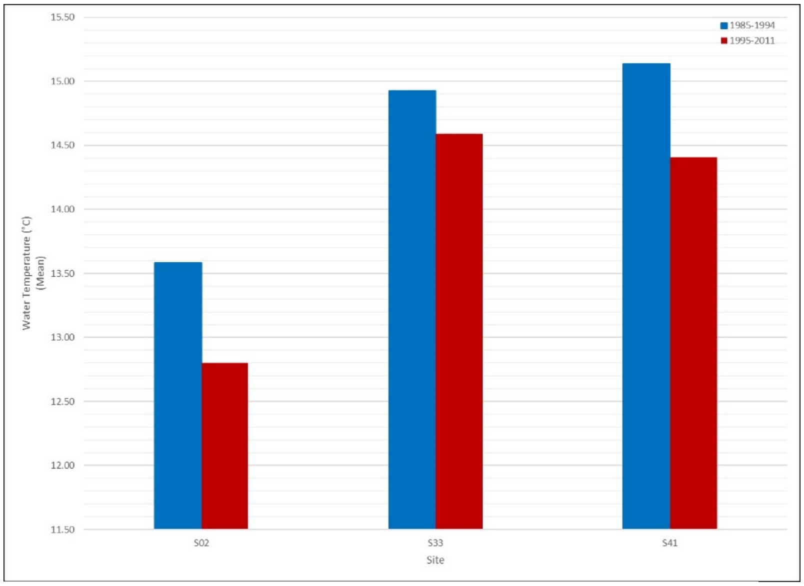


Figure 4.9.4 Comparison of mean water temperature from 1985-1994 and 1995-2011 for Buffalo River spring sites

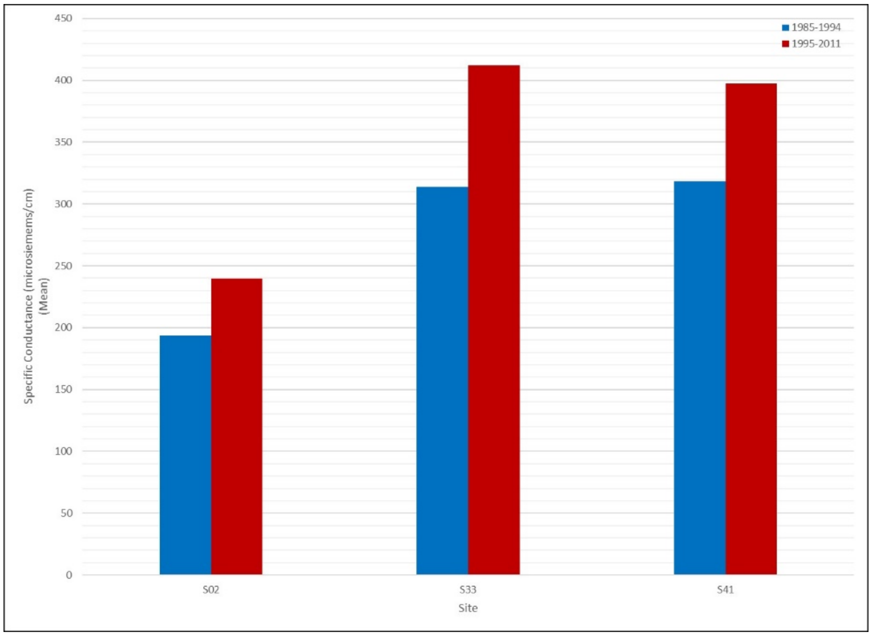


Figure 4.9.5 Comparison of mean specific conductance from 1985-1994 and 1995-2011 for Buffalo River spring sites

Between the 1985-1994 period (Mott, 1997) and the 1999-2011 period, mean pH values were similar at the three springs (Figure 4.9.6, and Figure 26 in Mott, 1997). Means at the three springs ranged from about 7.3 to 7.6 during the two time periods. Highest mean pH values were at Gilbert Spring between 1985-1994 and at Luallen Spring from 1999-2011; the mean pH of Gilbert Spring was 0.04 units lower than the mean pH of Luallen Spring from 1999-2011. Values of pH in springs in the Boston Mountains typically are lower (median=6.6) than values in springs in the Springfield Plateau (median=7.2) (Kresse and others, 2014).

Between the 1985-1994 period (Mott, 1997) and the 1995-2011 period mean dissolved oxygen concentrations were similar at two springs and increased at Luallen Spring (Figure 4.9.7). Mean concentration increased at S02 (Luallen Spring) from 8.85 to 9.87 mg/L and at S41 (Gilbert Spring) from 8.81 to 8.96 mg/L while decreasing at S33 (Mitch Hill Spring) from 8.33 to 8.08 mg/L.

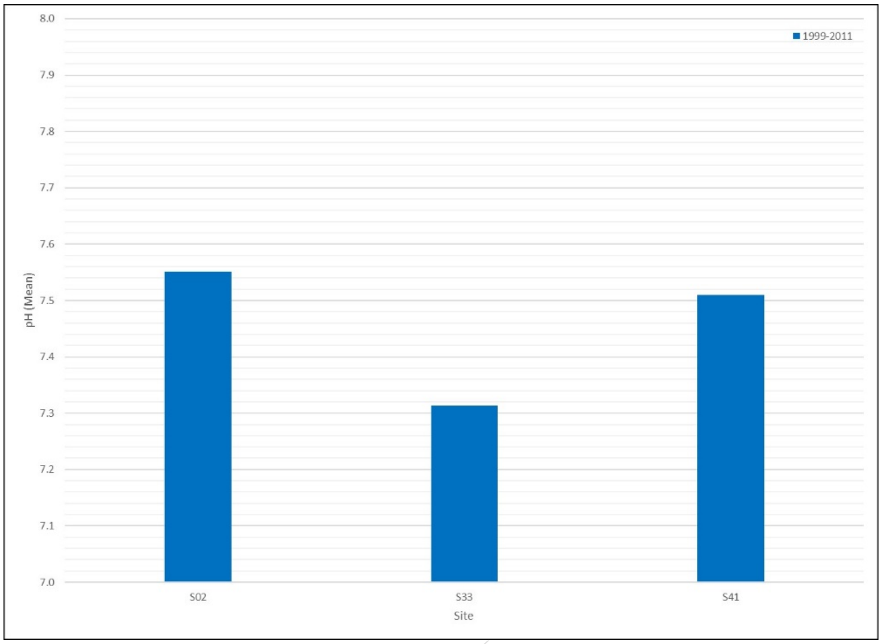


Figure 4.9.6 Mean pH values for Buffalo River spring sites from 1999-2011

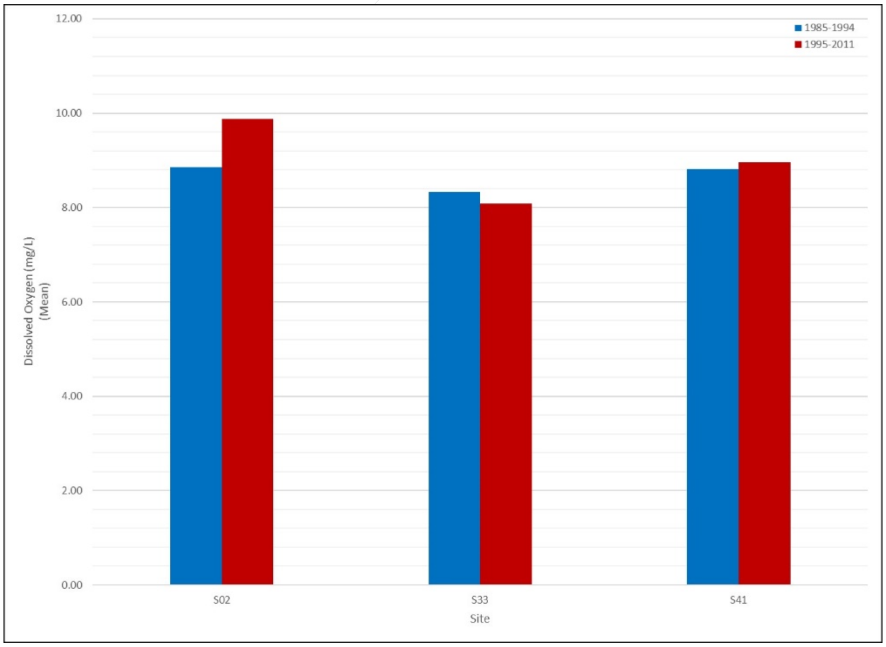


Figure 4.9.7 Comparison of mean dissolved oxygen concentration from 1985-1994 and 1995-2011 for Buffalo River spring sites

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5. Conclusions and Recommendations

5.3. Conclusions

The main purpose of this report is to present the results of water quality sampling on the Buffalo River and its tributaries from 1995-2011 and compare this data to data presented in historical water quality studies that evaluated data as early as 1985 to as late as 1998 (Mott, 1997; Mott and Luraas, 2004). The following conclusions can be made based on the data analyzed for this study:

1) During base-flow conditions, R02 (Ponca) continues to have the highest geometric mean and mean fecal coliform bacteria concentrations among the river corridor sites. The geometric mean fecal coliform bacteria concentration at R02 is approximately three times higher than the mean of the geometric means of the other eight sites. Similar findings were noted by Mott (1997).
2) A dense area of agricultural lands is adjacent to the Buffalo River between R01 (Wilderness Boundary) and R02 (Ponca) and is primarily used to support cattle operations. It has the highest acres of agriculture land per mile of river (126.2 acres/mile). Tributaries that flow across these fields, where cattle tend to loaf in summer months, are likely transporters of the animal waste and potentially create higher fecal coliform bacteria concentrations at R02.
3) Evaluation of the geometric mean of all base-flow conditions, river corridor samples for each year beginning in 1985, indicates that the geometric mean of fecal coliform bacteria concentrations generally increased with time. The geometric mean generally increased over time from 1985-1999, decreased through 2006, and then increased after 2006.
4) At river corridor sites, although base-flow data from 1995-2011 were insufficiently frequent to make an ultimate determination, it appears that the water quality standard for fecal coliform bacteria (geometric mean of 200 col/100 mL from at least five samples during a 30-day period, or a value for an individual sample of 400 col/100 mL) for primary contact seasons was being met, except at R02 (Ponca) where two concentrations exceeded 400 col/100 mL. However, it is important to note that concentrations for only 5 river corridor samples out of 491 collected during base-flow conditions between 1995-2011 were higher than 200 col/100 mL. Three of these five samples were collected at R02 (1999 and 2001) and the other two samples were collected at R06 (Gilbert) (2001) and R09 (Mouth) (2009).
5) At the tributary sites, although base-flow data from 1995-2011 were insufficiently frequent to make an ultimate determination, it appears that the water quality standard for fecal coliform bacteria for primary contact seasons generally was being met. However, it is important to note that concentrations for 33 of 1,141 tributary samples collected during base-flow conditions between 1995-2011 were higher than 200 col/100 mL. Twelve samples were collected at T17 (Water Creek) and T14 (Tomahawk Creek). The individual sample standard (400 col/100 mL) was exceeded once or twice at T02 (Ponca Creek), T05 (Little Buffalo River), T07 (Big Creek), T08 (Cave Creek), T10 (Calf Creek), T14 (Tomahawk Creek), and T17 (Clabber Creek).
6) Correlation analysis showed that tributary-site fecal coliform bacteria concentrations increased with increases in percent pasture land within each watershed.

7) During base-flow conditions, mean NO_3-N concentrations for river corridor sites for the sampling period of 1995-2011 ranged from 0.04 (R01, Wilderness Boundary) to 0.12 mg/L (R08 (Rush)). With the exception of R01 (Wilderness Boundary), mean concentrations were approximately 25% to 55% higher than concentrations measured from 1985-1994 (Mott, 1997).
8) Evaluation of the mean NO_3-N concentrations for all river corridor base-flow condition samples collected since 1985 indicates that the mean NO3-N concentrations generally increased with time.
9) For the 20 tributary sites sampled during base-flow conditions, the mean NO_3-N concentration of samples collected from 1995-2011 was less than 0.70 mg/L. T04 (Mill Creek) and T13 (Brush Creek) had the highest mean concentrations--each greater than 0.6 mg/L. Data collected during 1985-1994 (Mott, 1997) showed similar results with T04 and T13 having the highest mean concentrations of the sites, but with slightly lower mean concentrations between 0.4 and 0.5 mg/L.
10) A positive correlation was shown between mean NO_3-N concentrations of all samples collected at each river corridor site and the percent pasture land within the upstream watershed with NO3-N concentrations increasing as percent pasture lands increased. A similar correlation was shown between mean NO_3-N concentrations of all samples collected at each tributary site and the percent pasture land within the upstream watershed.
11) Mean PO_4-P concentrations for river corridor sites during base-flow conditions did not vary substantially and ranged from 0.007 (at several sites) to 0.009mg/L (R09, Mouth). The highest mean concentrations were associated with the four sites in the most-downstream part of the Buffalo River. Mean concentrations were slightly lower than those noted in Mott (1997).
12) A change in analytical methods in September 2003 that increased the minimum detection limit from 0.005 to 0.01 mg/L precluded analysis of temporal trend in PO_4-P concentrations between 1995-2011.
13) For 18 of the 20 tributary sites sampled during base-flow conditions, the mean PO_4-P concentration of samples collected from 1995-2011 was less than 0.020 mg/L. T10 (Calf Creek) and T13 (Brush Creek) had mean concentrations of 0.032 and 0.039 mg/L, respectively. Mott (1997) showed similar results when evaluating data from 1985-1994.
14) River corridor site mean turbidity values for samples collected during base-flow conditions were generally less than 2 NTU.
15) Tributary site mean turbidity values for samples collected during base-flow conditions were less than 2 NTU for most sites. The mean turbidity value for all base-flow samples analyzed at T02 (Ponca) was greater than three times the mean value from 1985-1994 (Mott, 1997).
16) Water temperature exceeded Arkansas water quality standards for 35 measurements at river corridor sites and 9 measurements at tributary sites from 1995-2011. Most of the exceedances of water temperature occurred in the Ozark Highlands at river corridor sites and few occurred in the Boston Mountains or at tributary sites. More than half of all measurements (31 of 60) made during June through August at river corridor sites in the Ozark Highlands exceeded the standard. At the corridor sites the number of exceedances and the maximum measured temperature generally increased in a downstream direction; no exceedances were recorded at sites R01 (Wilderness Boundary), R02 (Ponca), R03

(Pruitt), R04 (Hasty) and R05 (Woolum), and most exceedances were recorded at site R09 (Mouth). This would be expected as wetted stream width increases, effect of riparian shading decreases, and cooling effects of groundwater recharge decreases. At the tributary sites, the association between number of exceedances and drainage area was less consistent. However, fewer exceedances occurred at Boston Mountains sites (where the water temperature standard is higher) than at Ozark Highlands sites. Three of the five sites with exceedances were among the tributary sites with the largest drainage areas. Dissolved oxygen concentrations seldom exceeded water quality standards. Values of pH never exceeded standards.

17) Water quality was substantially different at the three sampled springs. The two springs in the Springfield Plateau in the Ozark Highlands had higher geometric mean fecal coliform bacteria concentrations, mean NO_3-N concentrations, mean temperature, and mean specific conductance. Mean NO_3-N concentrations increased through time at the Springfield Plateau springs and decreased at the spring in the Boston Mountains. Specific conductance increased substantially at the three springs compared to Mott (1997).

5.4. Recommendations

Implementation of the following recommendations will require a coordinated effort among Buffalo River watershed stakeholders including landowners; businesses; agriculture-based operations and industry; federal, state, and local government agencies; and non-governmental organizations (NGOs). Government agencies should include the National Park Service, U.S. Department of Agriculture Natural Resources Conservation Service, ADEQ, Arkansas Natural Resources Commission, Arkansas Game and Fish Commission, U.S. Department of Agriculture Farm Service Agency, U.S. Fish and Wildlife Service, and NGOs (including local watershed organizations and entities whose mission is protecting the Buffalo River).

1) Much of the Buffalo National River is within 100 miles of the Fayetteville-Springdale-Rogers metropolitan statistical area. The population of this area grew at an average rate of 2.6% per year between 2003 and 2013 (Northwest Arkansas Council, 2016). Pressures from population growth and associated development, visitor use, agricultural activities, and climate change suggest that stresses on the physical (including water quality) and biological components of the Buffalo National River will increase. Dependence on crisis management cannot protect the Buffalo River or its watershed from this future threat. It is important to develop and implement programs now that are proactive and consider economic development, environmental protection, land conservation, and restoration of impacted areas. A proactive approach can be initiated immediately by the formation of a Buffalo River Watershed (BRW) Planning Team to help implement voluntary, non-regulatory strategies. A BRW Planning Team that consists of entities described above should be formed to discuss and help to implement the following recommendations. An NGO should coordinate and facilitate the BRW Planning Team to ensure unbiased representation of all participants. This NGO should also seek funding to support the implementation of recommendations. The BRW Planning Team should also work with

the Beautiful Buffalo River Action Committee formed by the Governor of Arkansas in October of 2016; this committee consists of five state agencies (ADEQ, Department of Health, Natural Resources Conservation Commission, Department of Agriculture, and Department of Parks and Tourism) and is, among other tasks, to identify and address potential issues of common concern in the Buffalo River watershed.

2) To address the consistently higher fecal coliform bacteria concentrations at RO2 (Ponca) seen in this study and previous studies during base flow conditions, a program that supports agricultural best management practices (BMPs) that reduce both erosion and runoff from cattle operations should be developed for Boxley Valley. Implementation of the following BMPs can reduce fecal coliform, sediment and nutrient loadings to the Buffalo River and the small tributaries that flow across pastures adjacent to the Buffalo River:
    a. Restore 25 to 50 feet of riparian corridor along the small tributaries that run through the pastures in Boxley Valley using native grasses, shrubs, and trees appropriate for the ecoregion.
    b. Enhance the nutrient, bacterial, and sediment trapping abilities as well as the width of the riparian areas along the Buffalo River with native species of plants appropriate for the ecoregion.
    c. Assess both the river channel and small tributaries for stream instability and restore stream channel function and streambanks that are impacting, disturbing, or destabilizing riparian areas and pastures.
    d. Cattle do not have access to the Buffalo River, but they do have access to the small tributaries that run across the pastures to the river. Provide alternative shade and watering for cattle and restrict their access to these small tributaries.
    e. Evaluate forage cover and enhance cover with crops that grow during the winter months or with forage crops that develop a deep and well-integrated sod that holds sediment in place.
    f. Develop and implement rotational grazing practices.
    g. Provide one-on-one assistance and financial support to landowners to plan, design, and implement these practices. This should be developed through the BRW Planning Team.
3) T14 (Tomahawk Creek) fecal coliform bacteria concentrations were consistently higher than other tributaries in this study and in previous studies. A program that reduces both erosion and runoff from cattle operations should be developed and implemented for the Tomahawk Creek watershed that consists of the following:
    a. Restore 25 to 100 feet of riparian corridor along Tomahawk Creek and 25 to 50 feet along its tributaries where there are cattle operations.
    b. Apply voluntary BMPs, such as restrict cattle access to Tomahawk Creek and tributaries and provide alternative shade and watering sources.
    c. Assess Tomahawk Creek for stream instability and restore stream channel function and streambanks that are impacting, disturbing, or destabilizing riparian areas and pastures.

    d. Evaluate forage cover and enhance cover with crops that grow during the winter months or with forage crops that develop a deep and well-integrated sod that holds sediment in place.
    e. Develop and implement rotational grazing practices.
    f. Provide one-on-one assistance and financial support to landowners to plan, design, and implement these practices. This should be developed through the BRW Planning Team.
    g. Evaluate other potential sources of fecal coliform bacteria, such as septic tanks or community package plants, and implement measures to reduce their impacts if needed.

4) The rural nature of the Buffalo River watershed has resulted in numerous gravel roads in the watershed. An evaluation of gravel roads and associated engineering practices within selected tributary watersheds should be conducted to estimate sediment loadings and other impacts to water quality in the Buffalo River watershed. Based upon these evaluations, gravel road construction and maintenance BMPs should be encouraged and financially supported through grants.
5) Sources of fecal coliform bacteria and nutrients extend beyond cattle operations. The beauty of the Buffalo River watershed has attracted both new residents and tourists to the area for decades and has resulted in housing developments and recreation facilities that serve numerous people and communities. In the rural areas, wastewater is generally handled through septic tanks or outdated package plants that have not been maintained properly. Solutions to reduce the impacts of untreated or inadequately treated wastewater from communities, individual landowners, and the recreation industry need to be developed and implemented. Inadequately treated wastewater associated with outdated package plants and septic tanks in the Mill Creek watershed (T04) should be addressed immediately. A program should be developed through the BRW Planning Team to work with both Ponca and Mill Creek landowners to upgrade individual treatment systems (septic tank and leach fields) and outdated package plants to better quality or better technology. Other areas with similar problems in the watershed should be identified and addressed.
6) The potential impacts of a large swine CAFO in the Big Creek watershed (T06) on the water quality of the Buffalo River is a concern to the local watershed group, government agencies, and citizens throughout Arkansas and the United States. Data presented in this study were collected prior to the construction and the initial operation of the facility. Currently several entities are collecting water quality and other environmental data to monitor the water quality of Big Creek more closely and to evaluate potential impacts. The need for development and implementation of additional BMPs at a CAFO size swine operation in the Big Creek watershed should be evaluated. The additional BMPs may be needed to further minimize the impacts to the local ecology and water quality from this and similar facilities.
7) Measured water temperatures exceeded state water quality standards 44 times. Natural factors associated with wetted stream width would be expected to affect maximum stream temperatures. Potential changes in stream geometry (wider channels, shallower channels) affected by upstream and riparian land use changes could also affect these

temperatures. Stream geometry data are available for many of the water quality sites used for this study (Panfil and Jacobson, 2001; Petersen, 2004). Collection of updated stream geometry data and comparison to the historical data and data from other Boston Mountains and Ozark Highlands streams could provide insight about causation.

8) Because of the importance of the Buffalo National River to the citizens of Arkansas and the nation, the ecological significance of the waters of the Buffalo National River, and the growing stresses on the Buffalo National River it is important that the existing water quality monitoring be continued and not be reduced. It is also important that the National Park Service and other entities look for opportunities to cooperate in conducting appropriate scientific studies.

Literature Cited

Adamski, J.C., Petersen, J.C., Freiwald, D.A., and Davis, J.V., 1995, Environmental and hydrologic setting of the Ozarks Plateaus study unit, Arkansas, Kansas, Missouri, and Oklahoma: U.S. Geological Survey Water-Resources Investigations Report 94–4022.

American Public Health Association, American Water Works Association, and Water Environment Federation, 1992. Standard Methods for the Examination of Water and Wastewater, 18th edition: American Public Health Association.

Arkansas Department of Environmental Quality, 2016. Assessment Methodology for the Preparation of the 2016 Integrated Water Quality Monitoring and Assessment Report, accessed December 11, 2016 at https://www.adeq.state.ar.us/water/planning/integrated/assessment/pdfs/2016-assessment-methodology-draft-04apr16-305b.pdf

Arkansas Pollution Control and Ecology Commission, 2015. Regulation No. 2: Regulation Establishing Water Quality Standards for Surface Waters of the State of Arkansas: Arkansas Pollution Control and Ecology Commission, Little Rock, Arkansas.

Buffalo River Watershed Alliance, 2016. Advocates to Protect the Buffalo National River Watershed, accessed August 2016 at http://buffaloriveralliance.org/.

Chow, V. T., 1964. Handbook of Applied Hydrology, McGraw-Hill Book Company, New York, NY.

Cui, Yue, Mahoney, Ed, and Herbowicz, Teresa, 2013. Economic Benefits to Local Communities from National Park Visitation, 2011: Michigan State University, Department of Community, Agriculture, Recreation, and Resource Studies. East Lansing Michigan 48824-6446.

Davenport, M. A., and Smith R.M., 2007. Buffalo National River: A River Use Estimation Tool: Southern Illinois University, Human Dimensions Research Unit, Department of Forestry, Carbondale Illinois, 62901

Giese, John, Keith, Bill, Maner, Martin, McDaniel, Roland, and Singleton, Bob, 1987. Physical, Chemical, and Biological Characteristics of Least-Disturbed Reference Streams in Arkansas' Ecoregions, Volume II: Data Analysis: Arkansas Department of Pollution Control and Ecology.

Haley, B.R., Glick, E.E., Bush, W.V., Clardy, B.F., Stone, C.G., Woodward, M.B., and Zachry, D.L., 1993, Geologic map of Arkansas: U.S. Geological Survey, 1 sheet.

Hodges, S. W., 2012. Draft Climate Change Proposal to Investigate the Possible Effects of Climate Change on Fish Assemblages of Buffalo National River: National Park Service, Buffalo National River, Harrison, Arkansas 72601

Kresse, T.M., Hays, P.D., Merriman, K.R., Gillip, J.A., Fugitt, D.T., Spellman, J.L., Nottmeier, A.M., Westerman, D.A., Blackstock, J.M., and Battreal, J.L., 2014, Aquifers of Arkansas—Protection, Management, and Hydrologic and Geochemical Characteristics of Groundwater Resources in Arkansas: U.S. Geological Survey Scientific Investigations Report 2014–5149.

Mott, D.N., 1990. Effects of Cattle Pasture Runoff on the Water Chemistry of the Buffalo River, Boxley Valley, Arkansas: Arkansas Water Resources Center, Fayetteville, Arkansas.

Mott, D.N., 1997. Ten Years of Water Quality Monitoring, Buffalo National River, Arkansas: National Park Service, Buffalo National River, Harrison, Arkansas.

Mott, D.N., M. R. Hudson, and T. Aley, 2000. Hydrogeologic Investigations Reveal Interbasin Recharge Contributes Significantly to Detrimental Nutrient Loads at Buffalo National River, Arkansas: Proceedings of Annual Conference of Arkansas Water Resources Center.

Mott, D.N., and Jessica Luraas, 2004. Water Resources Management Plan: Buffalo National River, Arkansas. National Park Service, Buffalo National River, Harrison Arkansas.

National Centers for Environmental Information, 2016. Data Tools: 1981-2010 Normals, accessed September 30, 2016 at http://www.ncdc.noaa.gov/cdo-web/datatools/normals.

National Park Service, 1985. Water Quality Monitoring Plan, Buffalo National River: Water Resources Field Support Laboratory, Fort Collins, Colorado, Southwest Regional Office, Natural Resources Office, Santa Fe, New Mexico.

National Park Service, 2003. Draft Fire Management Plan/Draft Environmental Assessment: Buffalo National River, Arkansas.

National Park Service, 2015. "Management." National Park Service, U.S. Department of the Interior, accessed Mar. 2015 at <http://www.nps.gov/buff/learn/management/index.htm>.

Natural Resources Conservation Service, 1995. Buffalo River Tributaries, Watershed Plan Environmental Assessment: Natural Resources Conservation Service, Little Rock, Arkansas.

Northwest Arkansas Council, 2016. Data Summary-NWA: Northwest Arkansas Council, accessed October 2016 at http://www.nwacouncil.org/pages/data-summary-nwa/.

Panfil, M.S. and Jacobson, R.B., 2001. Relations Among Geology, Physiography, Land Use, and Stream Habitat Conditions in the Buffalo and Current River Systems, Missouri and Arkansas: U.S. Geological Survey Biological Science Report 2001-0005.

Petersen, J.C., 2004. Fish Communities of the Buffalo River Basin and Nearby Basins of Arkansas and Their Relation to Selected Environmental Factors, 2001-2002: U.S. Geological Survey Scientific Investigations Report 2004-5119.

Petersen, J.C., Adamski, J.C., Bell, Davis, J.V., Femmer, S.R., Freiwald, D.A., and Joseph, R.L., 1998, Water Quality in the Ozark Plateaus, Arkansas, Kansas, Missouri, and Oklahoma, 1992-95: U.S. Geological Survey Circular 1158.

Scott, H.D. and K.R. Hofer, 1995. Spatial and temporal analysis of the morphological and land use characteristics of the Buffalo River Watershed, Arkansas: Water Resources Center Publication number MSC-170, University of Arkansas, Fayetteville, Arkansas.

Stynes, D. J., 2011. Economic Benefits to Local Communities from National Park Visitation and Payroll, 2010: Michigan State University, Department of Community, Agriculture, Recreation, and Resource Studies. East Lansing Michigan 48824-1222.

Thornton, K.W., and Nix, J.F., 1985. Water Quality Monitoring Program, Buffalo National River, Boxley Valley, Arkansas: Ouachita Baptist University, Arkadelphia, Arkansas.

United States Department of Agriculture, 1988. Soil Survey of Newton County, Arkansas: United States Department of Agriculture Soil Conservation Service, Washington, D.C.