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Turbidity and Ion Concentrations Vary with Land Use and Underlying Geology at the West Fork of the White River

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ABSTRACT

The West Fork of the White River (WFWR) watershed in northwest Arkansas is a trans-ecoregion watershed and is experiencing land-use changes, especially in the downstream portion of the watershed. The entire 54-km long river has been on the State's 303(d) list of impaired waterbodies for turbidity, total dissolved solids (TDS), and sulfate for many years. The purpose of this study was to identify which part(s) of the river fail to meet applicable water quality standards (WQS) and to investigate possible sources of pollutants, whether human-caused or naturally occurring. Water samples were collected once or twice a month at 9 sites along the WFWR from June 2014 through June 2018 and analyzed for turbidity, TDS, sulfate, and chloride. Median turbidity values ranged from 1.8 to 10.8 NTU and generally increased from upstream to downstream ($p<0.05$). TDS, sulfate, and chloride also increased from upstream to downstream ($p<0.05$), with median concentrations ranging from 40.8 to 151.3 mg/L, 3.5 to 27.9 mg/L, and 3.2 to 5.5 mg/L, respectively. Human development (urban plus pasture land use) also increases in the watershed from upstream (19%) to downstream (39%). The two most downstream sites exceeded the limit for turbidity and TDS in over 40% of the samples collected, thus violating the applicable WQS. Sulfate concentrations exceeded the limit in over 60% of samples collected from the 5 most downstream sites, where the underlying geology becomes more limestone and shale dominant, a potentially important source of sulfate. In addition to analyzing water quality in the WFWR, we looked at a larger dataset of 119 sites in the Boston Mountains and Ozark Highlands ecoregions, compiled from the Arkansas Department of Environmental Quality online database. Turbidity, TDS, sulfate, and chloride concentrations were all significantly greater in the Ozark Highlands than the Boston Mountains ecoregion ($p<0.05$). Our data suggest that there are likely human and natural sources of elevated constituent concentrations in the WFWR, and water resource managers should consider these variables when reviewing assessment methodologies or targeting areas for remediation activities.

KEY WORDS

Turbidity, total dissolved solids, sulfate, chloride, water quality standard, watershed management

INTRODUCTION

Over 600,000 of the 1.1 million miles of streams assessed in the United States are identified as impaired, meaning they are unable to support one or more of their designated uses (USEPA, 2017). In the U.S., the Clean Water Act requires states to identify streams, rivers, and lakes to be placed on the 303(d) list of impaired waterbodies. States must develop water quality standards and assessment methodologies to evaluate waterbodies for a variety of pollutants. Sediments, turbidity, total dissolved solids (TDS), chloride (Cl), and sulfate (SO_4) are some of the common water-quality parameters listed for non-attainment across the U.S. (USEPA, 2018).

Excessive amounts of sediments and high turbidity can negatively impact water quality by changing the physical, chemical, and biological characteristics of streams and rivers. Sediment transport to drinking water supplies can reduce water storage capacity due to infill and result in increased treatment costs (Holmes, 1988). In streams, increased sediment and deposition can negatively impact aquatic life by reducing light penetration, filling in channels when deposited, and possibly releasing bound pollutants such as metals and nutrients. Sediment deposition can increase habitat homogeneity (Jones et al., 2012), reduce interstitial refugia for aquatic organisms (O'Callaghan et al, 2015), increase macroinvertebrate drift (Bilotta and Brazier, 2008) and clog gills of animals (Bruton, 1985; Bilotta and Brazier, 2008). All of this can result in changes in the biological community of a stream system (Fossati et al., 2001; Jones et al., 2015) and degradation of the waterbody's intended use(s).

Sediments and turbidity can be transported from the watershed or can originate from within the fluvial channel. Turbidity relates to catchment land use, where urban and agricultural land can increase turbidity in receiving streams (Ryan, 1991; Wood and Armitage, 1997; Brett et al., 2005). Urban areas might show a decrease in overland sediment transport due to large areas of impervious surfaces such as roads and parking lots (Wolman, 1967). However, urban land use indirectly influences sediment transport by increasing peak flows during storm events, leading to increased channel erosion (Trimble, 1997; Nelson and Booth, 2002), which can be the predominant source of sediments and turbidity in some streams (Simon and Klimetz, 2008; Mukundan et al., 2015). In fact, Van Eps et al. (2004) showed that stream bank erosion was the primary source of sediments to the West Fork of the White River, the focus of the current study.

Total dissolved solids (TDS) refers to all the dissolved materials in water, largely minerals, salts, and ions, and chloride and sulfate can make up a large proportion of TDS in waters. Increasing ion concentrations have been shown to change algal community structure in streams (Potapova and Charles, 2003), potentially affecting food web dynamics. Even low-level increases in dissolved ions might negatively impact stream macroinvertebrates due to osmoregulatory and physiological stress (Freitas and Rocha, 2011; Tyree et al., 2016). Increases in ionic concentrations definitely influence the biological community and ecosystem functions, but how these changes relate to the waterbody's designated use(s) is more challenging.

Dissolved ions naturally occur in streams and vary with watershed soils and geology (Griffith, 2014), but anthropogenic activities such as urban development and agriculture increase ions, especially chloride and sulfate, in surface waters (Herlihy et al., 1998; Zampella et al., 2007; Wright et al., 2011). Effluent discharges from industrial or municipal wastewater are sources of chloride and sulfate (Fitzpatrick et al, 2007). Chloride and sulfate concentrations in streams are also influenced by road salts, fertilizers, animal waste, and rainwater (Khatri and Tyagi, 2015).

In Arkansas, approximately 8,875 km of streams are listed as impaired, including the entire 54 km-long West Fork of the White River (WFWR). The WFWR is a major tributary to the White River, which forms the drinking water supply, Beaver Lake, for almost half a million people in northwest Arkansas. Turbidity, total dissolved solids (TDS), and sulfate violate the applicable WQS in the WFWR. The objectives of this study were to: (1) evaluate base-flow water quality from the headwaters to the most downstream portion of the WFWR; (2) compare this data against the applicable WQS to identify which part(s) of the stream actually violate the standards; and (3) consider possible sources of these problem pollutants, whether human-caused or naturally occurring. The goal of this paper is to help watershed managers target problem areas for improvement and allow regulators to make data-driven decisions on water-quality impairment issues.

METHODS

Study Sites

The West Fork of the White River (WFWR) watershed is a 322 km^2 sub-watershed of the Upper White River Basin, located in northwest Arkansas (Figure 1). The WFWR is approximately 54 km long, with headwaters near the small town of Winslow in the Boston Mountains ecoregion. The river flows north into the Ozark Highlands ecoregion where it enters into the White River in the more populated city of Fayetteville. The White River forms Beaver Lake, the drinking water supply for over 400,000 people in northwest Arkansas.

Water samples were collected at 9 sites in the WFWR (Figure 1). The 6 most upstream sites are located in the Boston Mountains, while the 3 most downstream sites are located in the Ozark Highlands ecoregion. Geology in the Boston Mountains is dominated by sandstone, limestone, siltstone, and shale (Woods et al., 2004). The Ozark Highlands consists of soluble and fractured geology and is dominated by shale, limestone, and dolomite (Woods et al., 2004). The karst topography of the Ozark Highlands allows for greater subsurface transfer of water and minerals to surface waters.

Land use in the WFWR watershed is predominately forested (66%), with approximately 20% pasture and 14% urban (arkansaswater.org, for 2006). Land use varies across sites (Table 1), where the

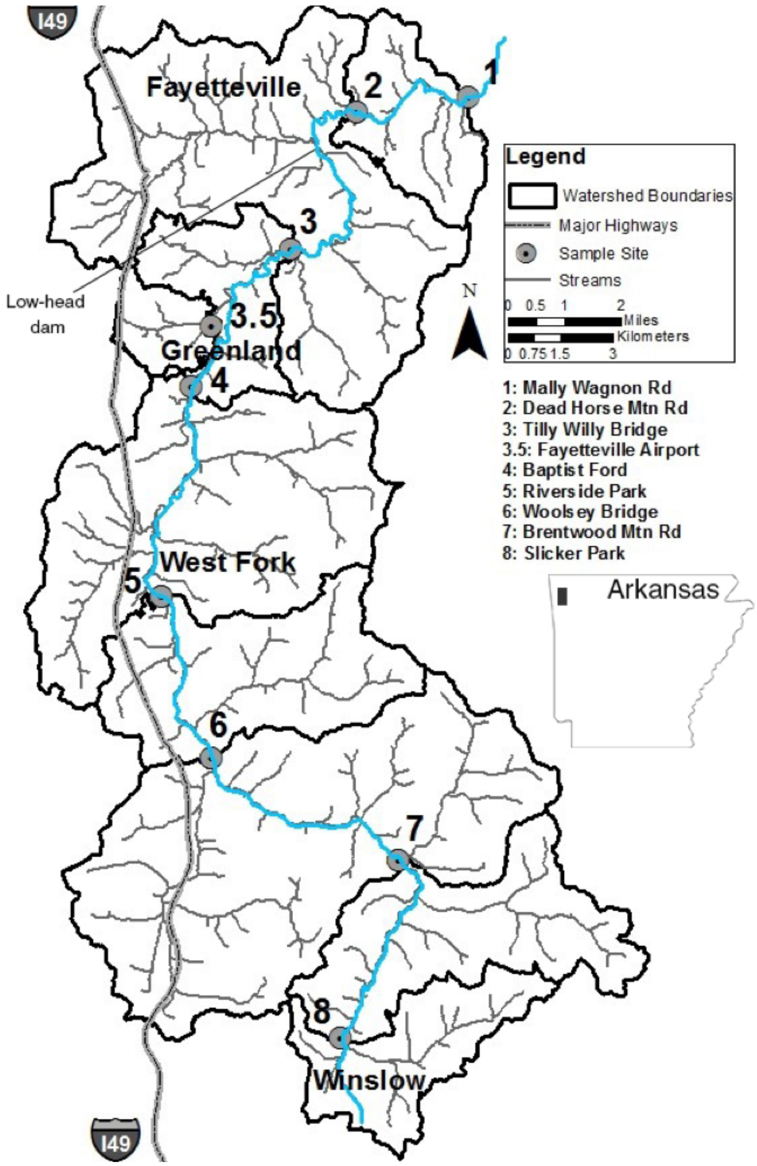

Figure 1. Map of AWRC study sites on the West Fork White River in northwest Arkansas.

upstream sites are closer to 70% forested and 5-7% urban. Downstream sites are less forested and more heavily urbanized, with approximately 50 and 13%, respectively. While there is one small municipal point-source wastewater discharge in the watershed, the downstream portion of the watershed also has several industrial sites permitted by the State for stormwater runoff discharges (ADEQ, 2018).

Water Sampling and Analysis

Water samples were collected 18 times per project year between July 2014 and June 2018 during base-flow conditions. Samples were collected from the thalweg using an alpha type sampler or manually from within the stream channel. Water samples were returned on ice to the Arkansas Water Resources Center Water Quality Lab (AWRC WQL, or Lab) and analyzed for turbidity (WTW Turb 550 Turbidity Meter), TDS (Mettler Toledo AX205), and sulfate and chloride (Thermo Scientific Dionex ICS-1600) according to standard methods (AWRC, 2018). The Lab is certified by the Arkansas Department of Environmental Quality (ADEQ) for the analysis of water samples, including all parameters analyzed for this project.

Turbidity, TDS, sulfate, and chloride for the WFWR study sites were evaluated against the applicable water quality standard (WQS) for Arkansas (APCEC, 2014). For turbidity, the WQS states that:

- The limit “should not be exceeded during base flow (June to October) in more than 20% of samples;
- and should not be exceeded during all flows in more than 25% of samples taken in not less than 24 monthly samples.” Here, “all flows” values apply to data collected throughout the year, including between June to October.
- The limit for turbidity is specific to ecoregion and months sampled, where the limit for the Ozark Highlands ecoregion is 10 and 17 NTU for “base” and “all flows”, respectively; the limit for the Boston Mountains ecoregion is 10 and 19 NTU for “base” and “all flows”, respectively.

The WQS for TDS, sulfate, and chloride is site specific to the WFWR and states that:

- the stream “will be listed as non-support when greater than 25% of samples exceed the applicable criteria.”
- The site-specific limit for TDS is 150 mg/L.
- The site-specific limit for chloride and sulfate is 20 mg/L.

Percent exceedances of the water quality limits were calculated and reported for turbidity, TDS, sulfate, and chloride.

In order to better understand how ecoregion might influence stream water quality, data was acquired from the ADEQ Water Quality Monitoring online database for an additional 110 sites throughout the Boston Mountains and Ozark Highlands ecoregions. The database was accessed in October 2018 and the date range searched was from June 1, 2014 through June 30, 2018. Data were used for a site if at least 8 observations were available for each parameter and these observations were collected over the course of at least 2 years. The geomeans were calculated for each site and used for subsequent analysis. Land use and land cover data for these additional 110 sites were estimated using the Model My Watershed application from the WikiWatershed initiative (Stroud Water Research Center, 2017).

Water quality data for the WFWR were log-transformed and then site means were compared using analysis of variance (ANOVA). Post-hoc tests were completed using the least significant difference (LSD) to test for differences across sites (Statistix 10.0). Relationships between water quality parameters and LULC variables were analyzed using linear regression (R v. 3.3.1). To test differences in water quality between ecoregions, an ANOVA was used on site geomean data (R v 3.3.1). All statistics were considered significant at alpha = 0.05.

RESULTS

Turbidity

Turbidity varied widely within and across all nine sites along the WFWR, ranging from 1 to 299 NTU. However, turbidity over 100 NTU was rarely observed during the flow conditions sampled at the WFWR (Figure 2a). Most of the values were less than 20 NTU, and only 4% of all the data was greater than 20 NTU across all sites.

Turbidity increased from upstream (geomean 2.9 NTU at Site 8) to downstream along the WFWR (ANOVA, p<0.01), with particularly high values at the two most downstream sites where geomeans were just above 10 NTU. Turbidity was not significantly different between sampling sites (Sites 3.5-8) within the Boston Mountains, except at site 3.5 where there was a small but significant increase in turbidity (Figure 2a). There was another small but significant increase when transitioning to the Ozark Highlands (Site 3). However, turbidity greatly increased as we moved downstream from site 3 (geomean 5.6 NTU) to 2 (geomean 10.2 NTU). The two most downstream sites had the greatest measured turbidity compared to all other sites along the WFWR (p<0.01).

The two most downstream sites were also the

Table 1. Information for AWRC study sites on the WFWR, including site ID, distance downstream (Dist. Down.), site description, coordinate location (Lat. and Long.), ecoregion (Eco.), and land use (forest = %F; pasture = %P; urban = %U; pasture plus urban = %P+U).

Site ID	Dist. Down. (km)	Site Description	Lat.	Long.	Eco.	%F	%P	%U	% P + U	Area (km^2)
1	45	Mally Wagnon Road	36.054	-94.083	OH	59.7	25.7	13.6	39.4	318.3
2	40	Dead Horse Mtn Road	36.051	-94.119	OH	60.8	24.9	13.4	38.3	303.1
3	32	Tilly Willy Bridge (CR69)	36.016	-94.141	OH	64.3	26.2	8.7	34.9	236.3
3.5	29	Fayetteville Airport	35.994	-94.163	BM	66	25.5	8	33.5	220.9
4	27	Baptist Ford	35.981	-94.174	BM	67.1	25.3	7.1	32.4	214.8
5	19	Riverside Park	35.928	-94.184	BM	71.3	22.5	6	28.5	157.1
6	13	Woolsey Bridge	35.887	-94.169	BM	71.6	22.9	5.4	28.3	125.3
7	6	Brentwood Mountain	35.859	-94.11	BM	68.5	25.8	5.6	31.4	47.9
8	0	Slicker Park	35.814	-94.13	BM	67.4	24.9	7.6	32.5	17.7

only sites that violated the applicable WQS (Figure 2a; Table 2). During base flow (samples collected between June 1 and October 31), the two most downstream sites exceeded the limit of 10 NTU in 47% or more of the samples collected; whereas, the limit was exceeded in 6% or less of the samples collected at the other sites. During all flows (i.e. samples collected year-round during seasonal baseflow), these two downstream sites exceeded the limit for the Ozark Highlands ecoregion of 17 NTU in less than 20% of the samples collected, which did not violate the applicable WQS. The limit (i.e. 19 NTU for the Boston Mountains ecoregion) for all flows was exceeded in 6% or less of the samples collected at each of the other sites.

At the WFWR, geomean turbidity values increased with increasing pasture plus urban land use (28-39%) within the watershed ($r=0.93$, $p<0.01$; Figure 3a). However, this relationship did not hold when looking at the larger dataset of all 119 sites within these ecoregions ($p=0.58$; Figure 3b), which spanned a larger range in land use (2-90% pasture plus urban). When sites were separated by ecoregion, there was not a significant relation between turbidity and the proportion of pasture plus urban land use within the stream's watershed in the Boston Mountains. But, there was a relatively weak decreasing relationship within the Ozark Highlands ($r=-0.33$, $p=0.02$; Figure 3b). Overall, the geomean turbidity values were significantly greater in the Ozark Highlands compared to the Boston Mountains across the 119 sites, where geomeans averaged 8.7 and 2.9 NTU, respectively ($p<0.01$).

Total Dissolved Solids

TDS concentrations were variable within and across sites, ranging from a low of 7.5 mg/L at the upstream site to a high of 266 mg/L downstream at the WFWR. TDS concentrations significantly increased from upstream (geomean 38.2 mg/L) to downstream (geomean 143 mg/L), and the biggest increase really occurred between Sites 5 (geomean 76.6 mg/L) and 4 (geomean 112.1 mg/L). TDS concentrations in the WFWR steadily increased moving downstream in the four most upstream sites, but concentrations generally leveled off at the five most downstream sites (Figure 2b). The TDS concentrations at WFWR sites were also positively correlated to percent pasture plus urban land use in the in the drainage area ($r=0.75$, $p=0.02$; Figure 3c).

While TDS concentrations were not statistically different between the five downstream sites, Sites 1 and 2 were the only sites that violated the applicable WQS. TDS concentrations exceeded the limit of 150 mg/L in 44 and 50% of the samples collected at these sites, respectively (Table 2). The other site (3) in the Ozark Highlands exceeded the limit in 25% of the samples collected, close to violating the standard limit in more than 25% of the samples collected. The two more downstream sites (3.5 and 4) in the Boston Mountains exceeded the TDS limit in 19-22% of samples collected, while the more upstream sites had TDS concentrations below the 150 mg/L limit in all samples collected.

The geomean TDS concentrations across all 119 sites showed an increasing relation with percent pasture plus urban land use in the watershed ($r=0.68$, $p<0.01$; Figure 3d). When separated by ecoregion, pasture plus urban land use in the catchment explained 31 and 17% of the variability in geomean TDS concentrations in the Ozark Highlands and Boston Mountains, respectively ($p<0.01$; Figure 3d). There was really a shift in TDS concentrations when pasture plus urban land use increased above 35% within the drainage area.

Geomean TDS concentrations at the WFWR sites were within the range observed in the dataset of 119 sites in the same ecoregions (26.6-312 mg/L). When looking at this larger dataset, there were significant differences between the ecoregions ($p<0.01$). The average geomean of TDS concentrations was greater in the Ozark Highlands (171 mg/L) compared to the Boston Mountains (90.4 mg/L), which is consistent with that observed in the WFWR watershed.

Sulfate

Sulfate concentrations were variable from upstream to downstream, as well as within a site, and these individual concentrations ranged from 1 mg/L at the upstream site to over 50 mg/L at the downstream sites (Figure 2c). Sulfate concentrations significantly increased from upstream (geomean 3.8 mg/L) to downstream sites (max geomean 27.9 mg/L) at the WFWR ($p<0.01$; Figure 2c). However, there appears to be an abrupt shift in sulfate concentrations between Sites 5 and 4. When geomeans were grouped by ecoregion in the WFWR, the average geomean concentration in the Ozark Highlands (25.5 mg/L) was two times greater ($p=0.05$) than that observed in the Boston Mountains (12.6 mg/L).

The only sites that violated the applicable WQS for sulfate concentrations were the five most downstream sites (Sites 1 through 4; Table 2). These sites exceeded the applicable limit of 20 mg/L for sulfate concentrations in 63% or more of the water samples collected at each site over the study period (Table 2). None of the 4 upstream sites (Sites 5 through 8) violated the applicable WQS, where the limit was exceed in only one sample at three sites over the study.

Sulfate concentrations at the WFWR increased with increasing pasture plus urban land use within the catchment (r=0.73, p=0.03; Figure 3e), although there were really two groups of data that separated between Sites 5 and 4. This positive relation between geomean sulfate concentrations and pasture plus urban land use in the catchment also was seen in the larger dataset of all 119 sites across the two ecoregions (r=0.59, p<0.01; Figure 3f), where the geomean sulfate concentrations ranged from 2 to 37 mg/L. When these data were separated based on ecoregions, pasture plus urban land use in the watershed explained 19 and 37% of the variability in geomean sulfate concentrations within the Ozark Highlands and Boston Mountains, respectively (p<0.01). The average of the geomean sulfate concentrations was significantly greater (p<0.01) in the Ozark Highlands (10.9 mg/L) compared to the Boston Mountains (5.3 mg/L). The spread in the geomean sulfate concentrations really increased when the catchment had more than 30% pasture plus urban land use within it.

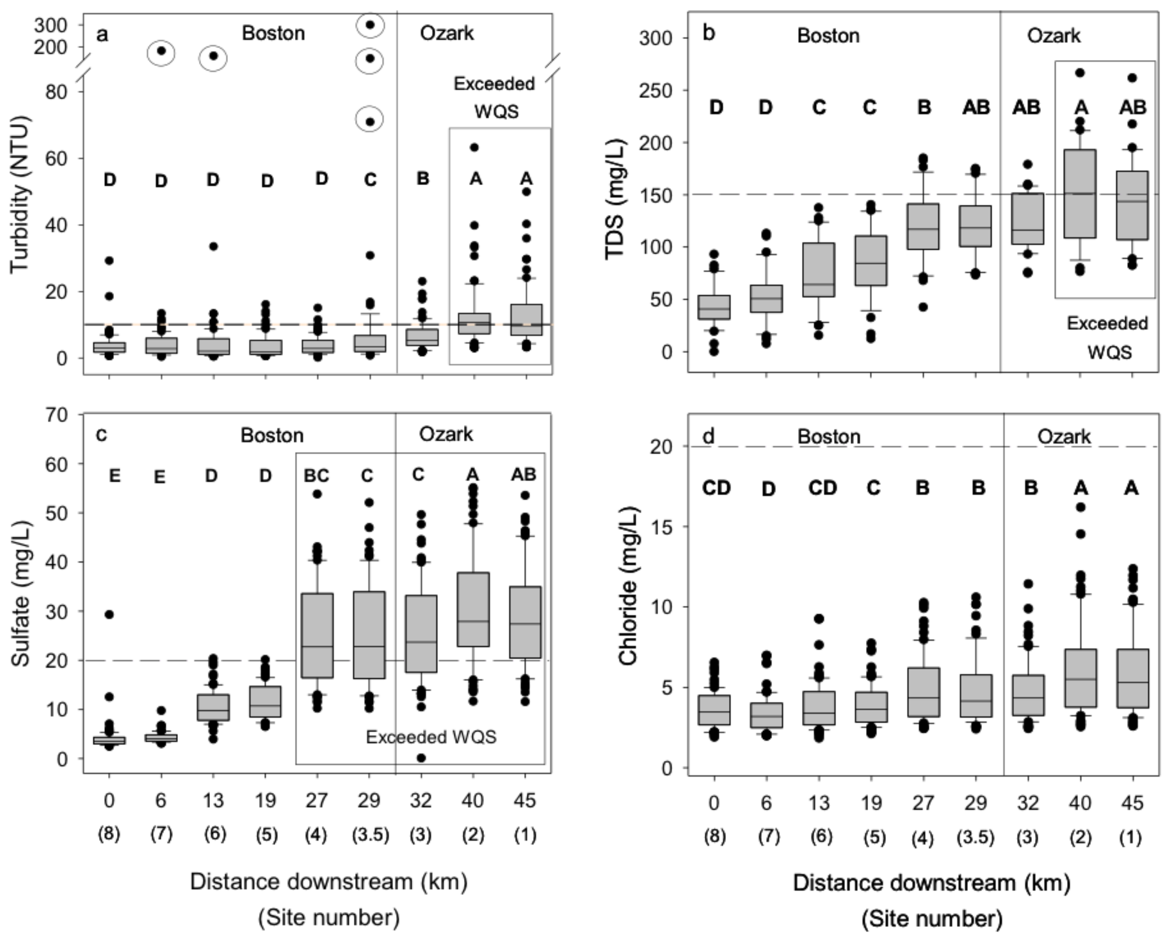

Figure 2. Box and whisker plots for (a) turbidity, (b) totals dissolved solids (TDS), (c) sulfate, and (d) chloride from upstream to downstream at the West Fork of the White River. The bottom and top of the box represents the 25th and 75th percentiles, respectively; the line inside the box represents the median value; the bottom and top whiskers represent the 10th and 90th percentiles, respectively; and the circles represent any observations that fall outside of the 10th and 90th percentile range. Horizontal dashed lines represent the relevant water quality standards (APCEC, 2015) for the Boston Mountains ecoregion (left of vertical line) and the Ozark Highlands ecoregion (right of vertical line). For turbidity, the line is drawn at the “base flow” standard (data collected June 1 – October 31), but all the data are shown. Circles around five observations for turbidity identify sample events where in-stream activities with heavy equipment took place. Capital letters represent statistical differences across sites (p<0.01).

Chloride

Chloride concentrations were generally low and ranged from 1.8 to 16.2 mg/L across all nine WFWR sites during the study period. Chloride concentrations increased from upstream to downstream along the WFWR where the greatest concentrations were observed at the two most downstream sites, Sites 1 and 2 ($p<0.01$; figure 2d). None of the sites along the WFWR exceeded the limit of 20 mg/L for chloride in any of the samples collected (Table 2).

In the WFWR watershed, geomean chloride concentrations ranged from 3.2 mg/L at the headwaters to 5.6 mg/L downstream, and these geomean concentrations significantly increased with increasing pasture plus urban land use in the drainage area ($r=0.86$, $p<0.01$; Figure 3g). Chloride concentrations were also significantly different between ecoregions within the WFWR, where average geomean concentrations were 4.9 and 3.5 mg/L in the Ozark Highlands and Boston Mountains, respectively ($p<0.01$). However, the geomean chloride concentrations across the WFWR were low relative to that observed more broadly across the ecoregions as seen in the 119 sites.

When data for all 119 sites were analyzed, geomean chloride concentrations also increased with increasing pasture plus urban land use in the watersheds ($r=0.68$, $p<0.01$; Figure 3h), where geomeans ranged from 1 to 40.5 mg/L across all sites. Percent pasture plus urban land use explained 46, 37 and 48% of the variability in geomean chloride concentrations in the entire dataset, the Ozark Highlands, and Boston Mountains, respectively ($p<0.01$; Figure 3h). The central tendency of the geomeans also differed significantly among ecoregions, where average geomean concentrations were 8.9 and 2.7 mg/L in the Ozark Highlands and Boston Mountains, respectively ($p<0.01$). The variability in geomean chloride concentrations with land use increased when pasture plus urban land use in the watershed was greater than 30%.

DISCUSSION

Turbidity

Stream turbidity increased with human activities (measured as pasture plus urban land use) in the WFWR watershed, although the change in land use was relatively small (28 to 39%). Several studies have shown increases in stream turbidity along an increasing gradient of human activity and development in the watershed (e.g., Trimble, 1997; Nelson and Booth, 2002; Brett et al., 2005). Even low level or small increases in human activity in the watershed have increased stream turbidity (i.e., agriculture plus urban land use ranged from 1 to 8%; Bolstad and Swank, 1997). The land use change in the WFWR watershed could be influencing turbidity in the water column.

However, the relation between stream turbidity and human land use did not hold across the larger database encompassing 119 stream sites across the Ozark Highlands and Boston Mountains ecoregions. The percent of human activity and development within these watersheds ranged from 3 to 90% (Figure 3), which was much broader than the change in the WFWR watershed. Interestingly, turbidity was either not related or slightly negatively correlated to the land use change across these 119 sites. This observation suggests that something else is likely related to the increasing turbidity in the WFWR as it flows downstream.

Much of the variability in stream turbidity was not explained simply by land use changes in the above-cited studies, suggesting that other factors and even natural sources cannot be discounted. Many states like Arkansas have ecoregion specific criteria, because ecoregions are defined by similar environmental characteristics such as climate, geology, and soil types (Omernik, 1987). The turbidity data across the 119 streams definitely support ecoregion specific criteria, because geomean turbidity levels were greater in the Ozark Highlands relative to the Boston Mountains. This is consistent with the downstream gradient in the WFWR, but it leaves us wondering why only the most downstream sites violated the WQS for turbidity.

In the WFWR, the primary component of turbidity is inorganic suspended solids, not organic matter (Cotton and Haggard, 2010). The violation in the WQS for turbidity is likely not from increased algal growth in the water column, although we do see slight increases in sestonic chlorophyll-a concentra-

Table 2. Percent exceedances of the constituent limit related to the applicable water quality standard (WQS) at sites along the West Fork of the White River. The horizontal dashed line represents the ecoregion divide between the Ozark Highlands (above) and the Boston Mountains (below). Bold values represent violations of the WQS. Constituent limits are given for turbidity (NTU), total dissolved solids (TDS; mg/L), sulfate (mg/L), and chloride (mg/L).

		Turbidity				
Site ID	**Site Description**	**Baseflow**	**All flow**	**TDS**	**Sulfate**	**Chloride**
Site 1	Mally Wagnon Road	47	19	44	77	0
Site 2	Dead Horse Mtn Road	59	17	50	79	0
Site 3	Tilly Willy Bridge (CR69)	6	6	25	66	0
Site 3.5	Fayetteville Airport	6	4	22	63	0
Site 4	Baptist Ford	0	0	19	65	0
Site 5	Riverside Park	0	6	0	1	0
Site 6	Woolsey Bridge	3	3	0	1	0
Site 7	Brentwood Mountain Road	1	3	0	0	0
Site 8	L.P. Jarnagan Ball Park	1	3	0	1	0
WQS Limits	Ozark Highlands	10	17	150	20	20
	Boston Mountains	10	19	150	20	20

tions (data not shown). The nutrient supply in the WFWR is relatively low, even at the most impacted site downstream (average SRP 0.003 mg/L and NO_3-N 0.228 mg/L, data not shown), and sestonic chlorophyll-a (2.0 µg/L; data not shown) would suggest that the WFWR is not eutrophic. So, the likely source of the turbidity would be from inorganic origin.

The shift in turbidity levels along the WFWR coincides with changes in the dominant riparian soils. Cotton and Haggard (2010) showed that riparian soils shift downstream, where the riparian areas around the two most downstream sites consist of Enders-Allegheny complex and Sloan, Razort, Taloka, and Pickwick silt loams. These soils have a higher erosivity index compared to most of the soils found further upstream in the riparian area. Thus, the increased turbidity might be natural due to the shift in soils or from fluvial channel erosion and instability where these soils are present.

In the WFWR, data showed that turbidity was elevated only at the two most downstream sites, spanning roughly 15% of the entire river. Yet, all 54 km have been on the State's 303(d) list of impaired waterbodies since 1998. That was, until, the State changed the way the WFWR is segmented. Ours and other studies provided scientific data that led to dividing the WFWR into two stream segments in 2018. The ADEQ segmented the river into two parts based on their identification of the ecoregion divide, between Sites 3 and 3.5 (ADEQ, 2018). Now only the downstream segment is listed for turbidity, supporting a more focused effort to address violations of the turbidity WQS.

However, the available information also suggests that the greater turbidity levels at the downstream sites, as well as across Ozark Highlands sites, might be driven by natural sources. This leaves the question, is a limit of 10 NTU appropriate for all sites in the Ozark Highlands? Regulatory agencies might consider a variance in the WQS for select streams or reaches where the source is possibly natural (i.e. soil type in the riparian areas).

TDS, Sulfate, and Chloride

Some of the anthropogenic sources of ions, particularly chloride and sulfate, in watersheds include wastewater treatment effluent, industry, fertilizers, animal manures, and even road deicers (Herlihy et al., 1998; Khatri and Tyagi, 2015). Many studies have shown that agricultural and urban land uses influence ion concentrations in streams, where streams draining agricultural and urban watersheds have significantly greater chloride and sulfate concentrations during base flow than primarily forested streams (Fitpatrick et al., 2007). For example, Wright et al. (2011) calculated mean chloride and sulfate concentrations at urban streams (30-70% urban land use) at 90 and 13 mg/L, respectively, which was almost twice as high as their reference streams (<5% urban land use). The changes in ion concentrations downstream in the WFWR and across the 119 ecoregion sites fits this pattern, where chloride and sulfate con-

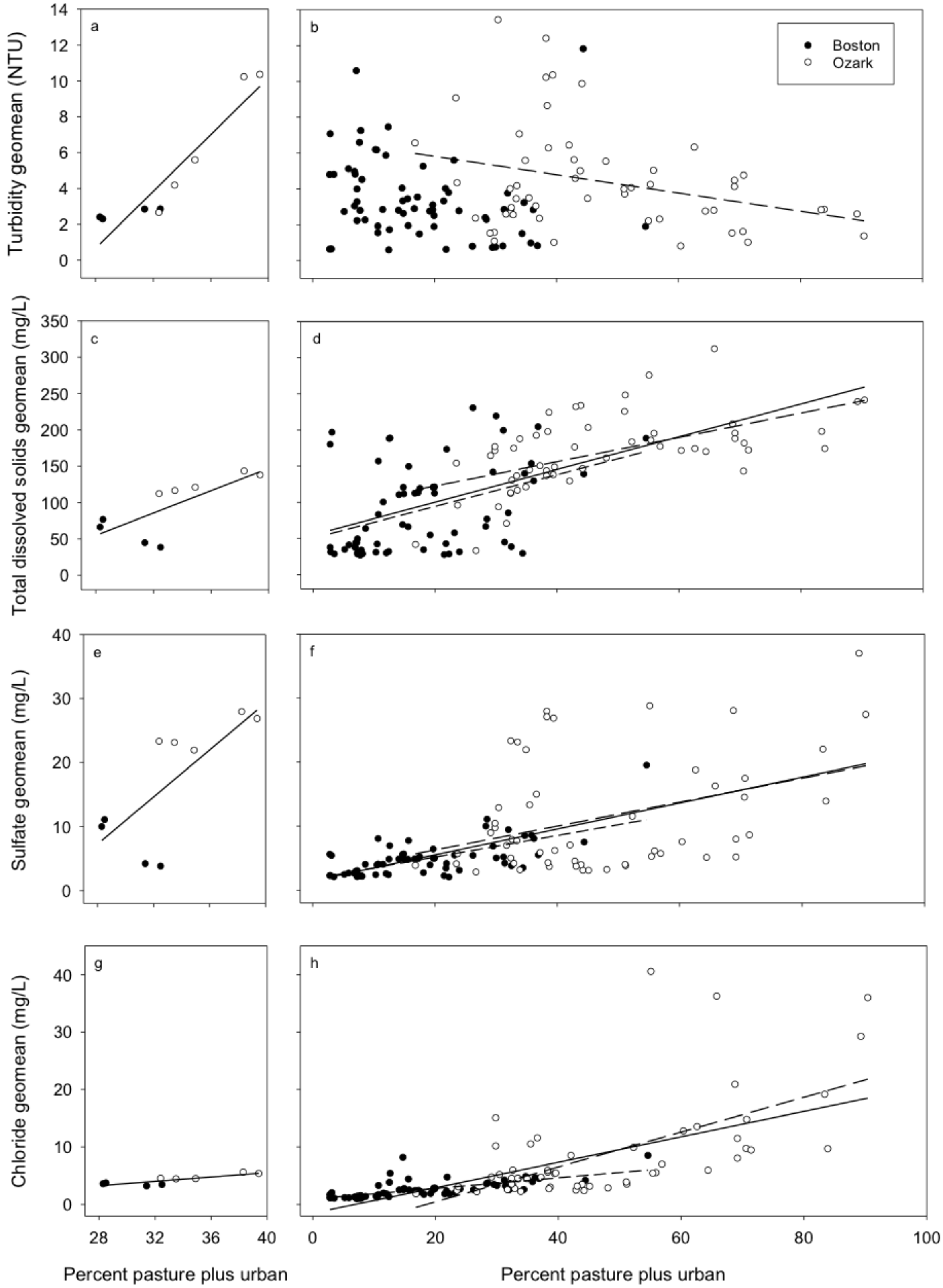

Figure 3. Geomean constituent concentrations versus percent pasture plus urban land use in the drainage area of study sites along the West Fork of the White River (WFWR). Panels show: (a) turbidity in the WFWR; (b) turbidity across all 119 sites; (c) total dissolved solids (TDS) in the WFWR; (d) TDS across all 119 sites; (e) sulfate in the WFWR; (f) sulfate across all 119 sites; (g) chloride in the WFWR; (h) chloride across all 119 sites. Linear regression lines are shown for significant relationships (p<0.05). Solid regression lines represent all the data, long-dashes represent data for the Ozark Highlands, and short-dashes represent data for the Boston Mountains.

centrations both increase with human activity and development in the watershed.

Chloride is naturally present in streams, and the magnitude of the concentration does vary with the underlying geology. But, chloride is an excellent conservative hydrologic tracer because it does not react physico-chemically in most freshwaters. That is why this ion often has a strong correlation to anthropogenic sources in watersheds, whether it be a signal of wastewater effluent in streams (MartÍ et al., 2004; Haggard et al., 2005) or nonpoint sources from the landscape (e.g., deicers; Khatri and Tyagi, 2015). The sites along the WFWR did not violate the WQS for chloride, but chloride concentrations at the WFWR and across the 119 sites in the Ozark Highlands and Boston Mountains increased with pasture plus urban land use.

Rock weathering of underlying geology can influence mineral and ion concentrations of surface waters, especially at base flow when groundwater is the major source of flow. TDS and chloride concentrations gradually increased downstream along the WFWR (Figure 2), but sulfate showed an abrupt increase between Sites 4 and 5, which is five or ten km upstream of the ecoregion divide. This suggests that there may be a natural characteristic at play as the WFWR flows downstream. Indeed, King et al. (2002) developed a geologic map of the West Fork quadrangle, which brackets upstream of Site 6 and just downstream of Site 3.5, and includes the abrupt shift in sulfate concentrations (Figure 4). Their map shows a distinct change in the underlying geology near and just downstream of Site 5, where bedrock becomes more limestone and shale dominant, especially along the river corridor. Relatively high sulfate concentrations can be found in streams and rivers in areas where the underlying geology is comprised of limestone (Khatri and Tyagi, 2015) and shale (Cerling et al., 1989). The abrupt increase in sulfate concentrations at the WFWR might be from a natural shift in the underlying geology.

The entire WFWR has been on the State's 303(d) list of impaired waterbodies for TDS and sulfate since at least 2010. After evaluating data from this study, among others, ADEQ segmented the WFWR in 2018. The segment divide occurs just downstream of Site 3.5, which is five to ten km downstream from the shift in underlying geology along the river corridor. Now only the downstream portion is listed as impaired for TDS and sulfate, while the upstream portion is still listed for sulfate (ADEQ, 2018).

A sulfate limit of around 20 mg/L might be appropriate if the intent of the WQS is to preserve reference conditions in the WFWR. However, the limit should also consider ecoregion divide, and even go further to identify variations in underlying geology. In the case of the WFWR, perhaps the ecoregion boundary should be moved to align with the abrupt shift we see in underlying geology, where high sulfate materials like limestone and shale dominate. If the divide is re-drawn where geology changes, then the river might be more appropriately segmented by ecoregion. The sulfate limit could then be adjusted to reflect the naturally higher concentrations expected in the Ozark Highlands compared to the Boston Mountains.

The WFWR is designated for primary and secondary contact recreation; domestic, agricultural, and industrial water supplies; and aquatic life. The aquatic life use is often considered the most sensitive to increases in sulfate concentrations compared to other designate uses, and thus is the basis of the WQS in the WFWF (personal communication, ADEQ). We know that excessive sulfate and TDS concentrations can have negative effects on aquatic life, including increased osmoregulatory stress and toxicity related to metabolic byproducts (Hart et al., 1991; Hassell et al., 2006; Johnson et al., 2015; Tyree et al., 2016).

If the intent of the WQS for sulfate is to protect aquatic life, then the limit of 20 mg/L might be quite low. Sulfate concentrations can be as high as 129 to 262 mg/L and still protect the most sensitive species of fish, macroinvertebrates, and algae (Soucek and Kennedy, 2005; Elphick et al., 2010; Table 3). In the WFWR, the greatest geomean sulfate concentration was 27.9 mg/L at site 2, with a maximum observed value of 55.1 mg/L, well below the thresholds seen in the above-mentioned studies. Further, other designated uses have sulfate thresholds near the upper range for aquatic life, and even higher thresholds for industrial, irrigation, and some livestock uses (Table 3). TDS and chloride concentration thresholds to protect various designated uses are also much higher than the concentrations observed in the WFWR (Table 3; Figure 2).

CONCLUSIONS

Water quality changes from upstream to downstream in the WFWR, where turbidity, TDS,

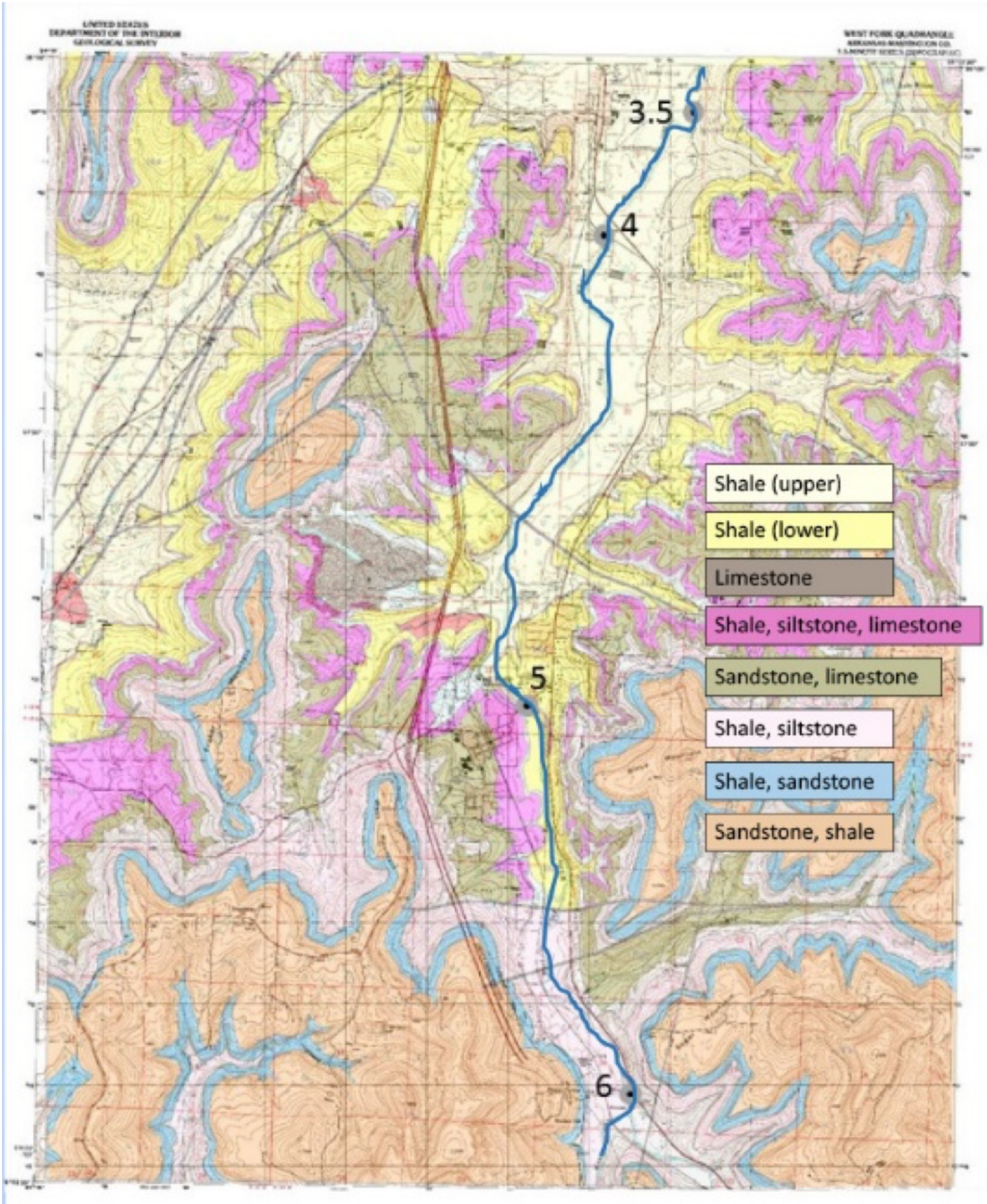

Figure 4. Map of the bedrock geology of the West Fork quadrangle, adapted from King et al. (2002). The blue line represents the West Fork White River (WFWR), which flows from south to north. The dots with numbers show sampling sites and the ecoregion divide is between Site 5 and 4.

Table 3. Threshold concentrations for TDS, Sulfate, and Chloride for the given designated use. Table includes the potential impact of exceeding the thresholds and the literature sources are listed.

Literature Thresholds					
Designated Use	**Impact**	**TDS (mg/L)**	**Sulfate (mg/L)**	**Chloride (mg/L)**	**Sources**
Aquatic life	Toxicity	-	129-262*	-	Soucek and Kennedy, 2005; Elphick et al., 2010
Domestic	Taste; Laxative	500	250	250	USEPA, 2018; APCEC, 20XX
Industrial	Salinity	1000	500	-	Driscoll et al., 2002
Poultry	Flushing, toxicity	-	200	150	Austin et al., 2016
Cattle	Laxative, toxicity	1000-2500	500	1500	Austin et al., 2016b
Swine	Laxative, toxicity	3000	1000	250	Austin et al., 2016c
Irrigation	Salinity	-	300	142	Austin et al., 2016d

*range is for protection of the most sensitive species

sulfate, and chloride concentrations increase as we move downstream. The entire 54-km long WFWR has long been on the State's 303(d) list of impaired waterbodies for turbidity, TDS, and sulfate. But, most of the WFWR had constituent concentrations that were within the allowable WQS limits. The results of our monitoring study led ADEQ to segment the river into two parts, such that the upstream portion has been removed from the list of impaired waterbodies for turbidity and TDS.

It can be hard to parse out the sources of increased turbidity, TDS, and sulfate in the WFWR. Our results suggest that, while these water-quality variables increase with increasing human land use (e.g. pasture plus urban), riparian soil types and underlying geology might also play an important role in the increasing concentrations we see. Watershed managers should consider the potential natural variability in constituent sources to waterways, such as variability due to shifts in ecoregion designation. Further, when a river spans multiple ecoregions, the boundary should be drawn based on known characteristics, particularly underlying geology in the case of the WFWR. If the ecoregion boundary was drawn where the shift in underlying geology occurs, then the upstream portion of the WFWR would also be removed from the 303(d) list for sulfate.

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