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Natural Characteristics and Human Activity Influence Turbidity and Ion Concentrations in Streams

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Abstract: All 54 km of the West Fork of the White River (WFWR) were on Arkansas's 303(d) list of impaired waterbodies for turbidity, total dissolved solids (TDS), and sulfate for many years. This study identifies which river segments fail to meet applicable water quality standards (WQS) and investigates possible anthropogenic or natural sources of pollutants. We also evaluated a larger dataset of 119 sites in the Boston Mountains and Ozark Highlands ecoregions, compiled from the Arkansas Department of Environmental Quality online database. In the WFWR, water samples were collected once or twice a month at nine sites from June 2014 through June 2018. Median values for turbidity, TDS, sulfate, and chloride ranged from 1.8 to 10.8 NTU, 40.8 to 151.3 mg/L, 3.5 to 27.9 mg/L, and 3.2 to 5.5 mg/L, respectively, and generally increased from upstream to downstream ($p < 0.05$). Violations of the water quality standard for the parameters of interest varied by site, but generally occurred in the downstream portion of the WFWR, where land use, riparian soils, and underlying geology change. In the larger dataset, turbidity, TDS, sulfate, and chloride concentrations were all significantly greater in the Ozark Highlands than the Boston Mountains ecoregion ($p < 0.05$). Anthropogenic activities influence dissolved ion concentrations across these study sites, while geology and riparian soils may be important factors for differences in sulfate and turbidity.

Keywords: *total dissolved solids, sulfate, chloride, water quality standard, watershed management*

Research Implications

- Sulfate concentrations in the West Fork White River (WFWR) abruptly increased where primary and secondary shales dominate the subsurface geology along the river corridor, aligning with river sections that exceeded the State's water quality standard (WQS).
- Site-specific WQSs in streams should consider changes in underlying geology to account for chemical contributions from these natural sources.
- Base-flow turbidity levels were relatively high at the two most downstream sites on the WFWR, where the natural riparian soils had high erositivity indices and thus a natural tendency to contribute inorganic solids to the stream.
- WQSs for turbidity and subsequent plans to address exceedances should consider riparian soil type and erosivity.
- Watershed land use and underlying geology influence physico-chemical properties of streams.

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 (WQS) and assessment methodologies to evaluate waterbodies for a variety of pollutants. Sediments, turbidity, total dissolved solids (TDS), sulfate, and chloride are some of the common water quality parameters listed for non-attainment across the U.S. (USEPA 2018a).

Excessive amounts of sediment and high levels of 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 can negatively impact aquatic life by reducing light penetration, filling channels, 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 (WFWR), the focus of the current study.

Sulfate and chloride make up a large portion of the dissolved minerals, salts, and ions in water. 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 agricultural activities can increase ion concentrations, especially sulfate and chloride, 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 sulfate and chloride (Fitzpatrick et al. 2007). Sulfate and chloride 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 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, TDS, and sulfate concentrations 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 these data against the applicable WQS to identify which part(s) of the stream actually violate the standards; and 3) consider possible landscape or in-stream 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. Here, we point out how these decision-makers should consider underlying geology and land use, among other considerations, when addressing water quality impairments.

Methods

Study Sites

The WFWR watershed is a 322 km^2 sub-watershed of the Upper White River Basin, 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. Of the nine sites where samples were collected, the six most upstream sites are located in the Boston Mountains, while the three 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 consist of soluble and fractured geology and are dominated by shale, limestone, and dolomite (Woods et al. 2004). The karst topography of the Ozark Highlands allows for net subsurface transfer of water and minerals to surface waters (Hays et al. 2016).

Land use in the WFWR watershed is predominately forested (66%), with approximately 20% pasture and 14% urban (ANRC 2018). Land use varies across sites (Table 1; Figure 1), where percent forest generally decreases and percent urban generally increases from upstream to downstream. While there is one small municipal point-source wastewater discharge in the watershed (design flow is 0.1 million gallons per day), 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

In this study, water samples were collected 18 times per year for four years at nine sites along the WFWR during base-flow conditions (see Figure 1). The sample collection schedule met or exceeded the requirements for sample frequency and duration needed to properly evaluate the WQS. 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 WQS for Arkansas (APCEC 2015). 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.
- 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 sulfate and chloride is 20 mg/L.

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

In a separate analysis to better understand how ecoregion might influence stream water quality, data were 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 eight observations were available for each parameter and these observations were collected over the course of at least two years. The geometric means were calculated for each site in order to reduce the influence of outliers and used for subsequent analysis. Land use and land cover (LULC) data for these additional 110 sites were estimated using the Model My Watershed application from the

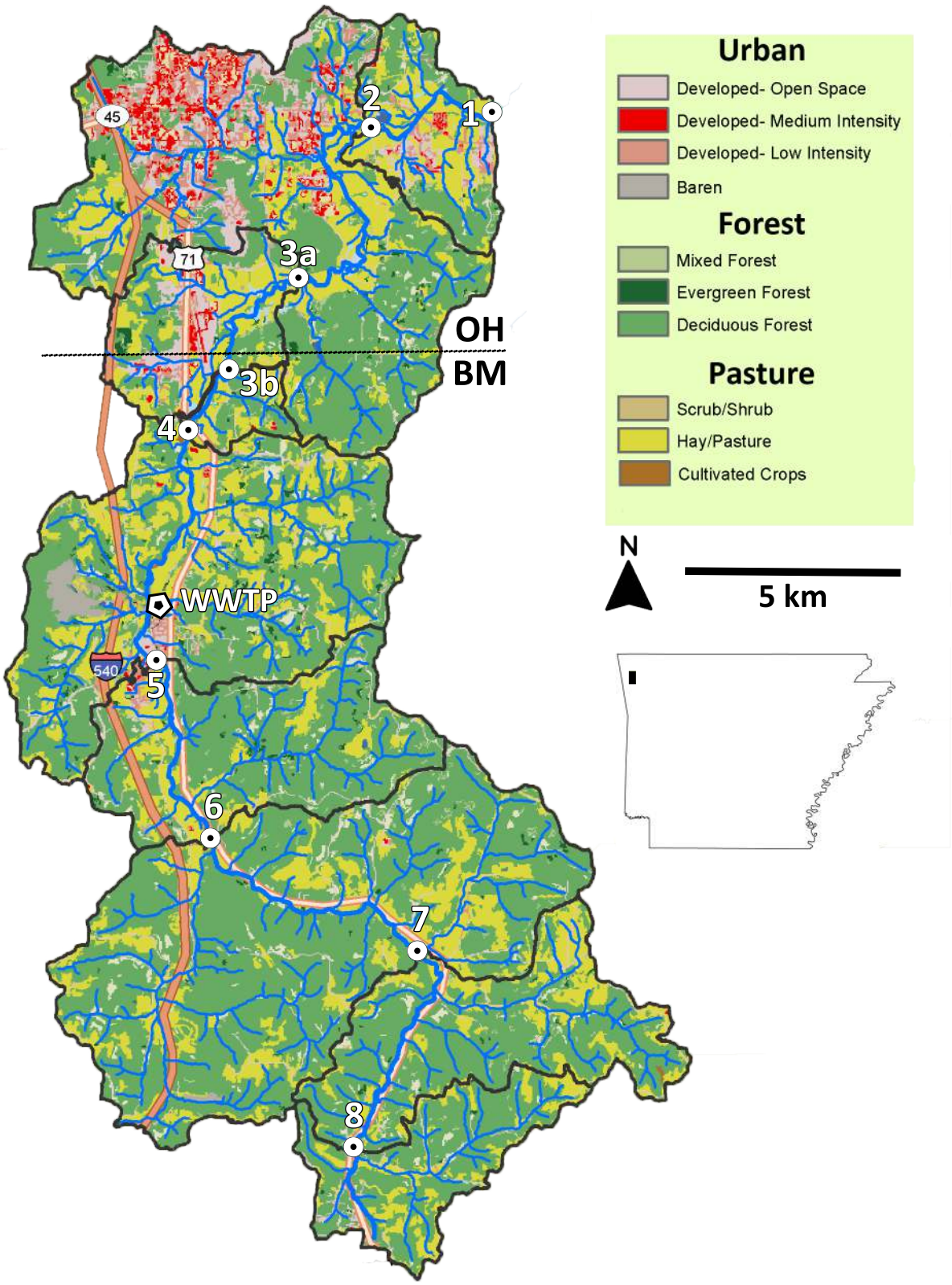

Figure 1. Map of AWRC study sites on the West Fork White River in northwest Arkansas, land use land cover, and delineations of site drainages. Sites are indicated by white circles with inner black dots; the West Fork wastewater treatment plant is indicated by a white pentagon with inner black pentagon; and the ecoregion boundary is indicated by a dotted line, with Ozark Highlands (OH) and Boston Mountains (BM) labels provided.

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	36.0539	-94.0833	OH	59.7	25.7	13.6	39.4	318.3
2	40	Dead Horse Mtn Road	36.0506	-94.1189	OH	60.8	24.9	13.4	38.3	303.1
3a	32	Tilly Willy Bridge (CR69)	36.0158	-94.1408	OH	64.3	26.2	8.7	34.9	236.3
3b	29	Fayetteville Airport	35.9944	-94.1628	BM	66.0	25.5	8.0	33.5	220.9
4	27	Baptist Ford	35.9814	-94.1739	BM	67.1	25.3	7.1	32.4	214.8
5	19	Riverside Park	35.9281	-94.1844	BM	71.3	22.5	6.0	28.5	157.1
6	13	Woolsey Bridge	35.8867	-94.1692	BM	71.6	22.9	5.4	28.3	125.3
7	6	Brentwood Mountain	35.8594	-94.1100	BM	68.5	25.8	5.6	31.4	47.9
8	0	Slicker Park	35.8144	-94.1300	BM	67.4	24.9	7.6	32.5	17.7

WikiWatershed initiative (Stroud Water Research Center 2017). Land use classifications were condensed into three categories – urban, forest, and pasture. There is essentially no row-crop agriculture in the watershed (less than 0.1% at all sites). Grassland is grouped with pasture, where grassland across sites ranges from 2-3%, while pasture alone ranges from 20-24% across sites.

Water quality data for the WFWR were log-transformed to reduce skewness of the data prior to the 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 Core Team 2016; v. 3.3.1). Although we collected samples during base-flow conditions where groundwater may influence in-stream water quality, McCarty and Haggard (2016) show that water quality during base flow can be a reliable metric to evaluate land-use impacts. To test differences in water quality between ecoregions, an ANOVA was used on site geometric mean data (R Core Team 2016; 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 were greater than 20 NTU across all sites.

Turbidity increased from upstream (geometric mean 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 geometric means were just above 10 NTU. Turbidity was not significantly different between sampling sites (Sites 3b through 8) within the Boston Mountains, except at Site 3b 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 3a). However, turbidity greatly increased as we moved downstream from Site 3a (geometric mean 5.6 NTU) to Site 2 (geometric mean 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 only sites that violated the applicable WQS (Table 2; Figure 2a). During base flow, these 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, 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, geometric mean 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 does not exist 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 geometric mean turbidity values were significantly greater in the Ozark Highlands compared to the Boston Mountains across the 119 sites, where geometric means 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 (geometric mean 38.2 mg/L) to downstream (geometric mean 143 mg/L), and the biggest increase occurred between Sites 5 (geometric mean 76.6 mg/L) and 4 (geometric mean 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 the WFWR sites were also positively correlated to percent pasture plus urban land use 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 (3a) 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 (3b 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 geometric mean 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 geometric mean TDS concentrations in the Ozark Highlands and Boston Mountains, respectively ($p < 0.01$; Figure 3d). There was a change in TDS concentrations when pasture plus urban land use increased above 35% within the drainage area.

Geometric mean TDS concentrations at the WFWR sites were within the range observed in the dataset of 119 sites in the same ecoregions (26.6 to 312 mg/L). When looking at this larger dataset, there were significant differences between the ecoregions ($p < 0.01$). The average geometric mean 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 in the WFWR 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 (Site 8) to over 50 mg/L at the downstream sites (Sites 1 and 2; Figure 2c). Sulfate concentrations significantly increased from upstream (geometric mean 3.8 mg/L) to downstream sites (maximum geometric mean 27.9 mg/L) at the WFWR ($p < 0.01$; Figure

2c). However, there appears to be an abrupt change in sulfate concentrations between Sites 5 and 4. When geometric means were grouped by ecoregion in the WFWR, the average geometric mean 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 four upstream sites (Sites 5 through 8) violated the applicable WQS, where a total of only three exceedances occurred across these sites during 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 geometric mean sulfate concentrations and pasture plus urban land use in

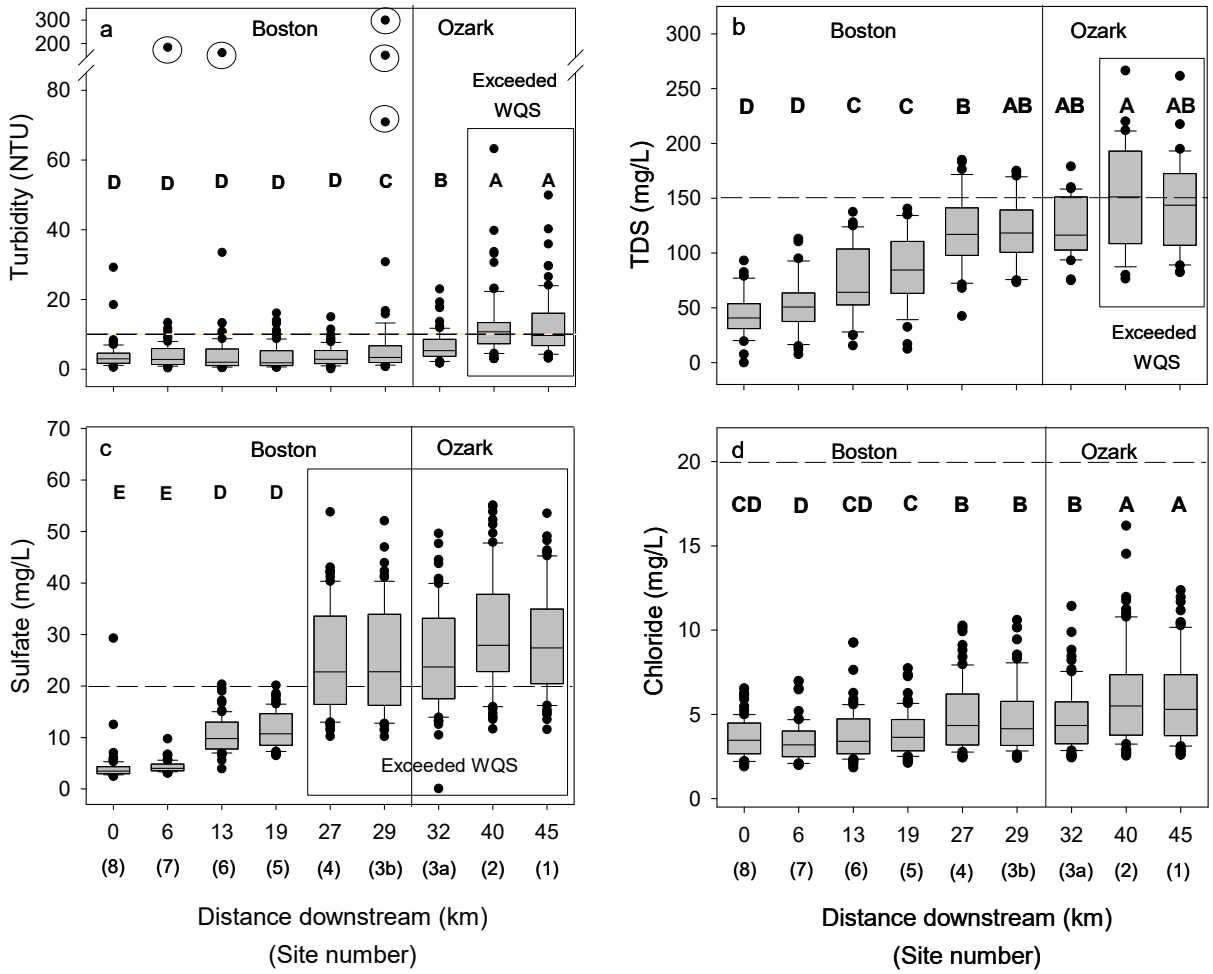

Figure 2. Box and whisker plots for (a) turbidity, (b) totals dissolved solids (TDS), (c) sulfate, and (d) chloride from upstream to downstream at the West Fork of the White River. The bottom and top of the box represents the 25th and 75th percentiles, respectively; the line inside the box represents 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 ($p < 0.01$).

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**	**Base flow**	**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 3a	Tilly Willy Bridge (CR69)	6	6	25	**66**	0
Site 3b	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

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 geometric mean sulfate concentrations ranged from 2 to 37 mg/L. When these data were separated based on ecoregion, pasture plus urban land use in the watershed explained 19 and 37% of the variability in geometric mean sulfate concentrations within the Ozark Highlands and Boston Mountains, respectively ($p < 0.01$). The average of the geometric mean 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 geometric mean sulfate concentrations increased when the catchment had more than 30% pasture plus urban land use within it.

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, geometric mean chloride concentrations ranged from 3.2 mg/L at the headwaters to 5.6 mg/L downstream, and these geometric mean 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 geometric mean concentrations were 4.9 and 3.5 mg/L in the Ozark Highlands and Boston Mountains, respectively ($p < 0.01$). However, the geometric mean 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, geometric mean chloride concentrations also increased with increasing pasture plus urban land use in the watersheds ($r = 0.68$, $p < 0.01$; Figure 3h), where geometric means ranged from 1 to 40.5

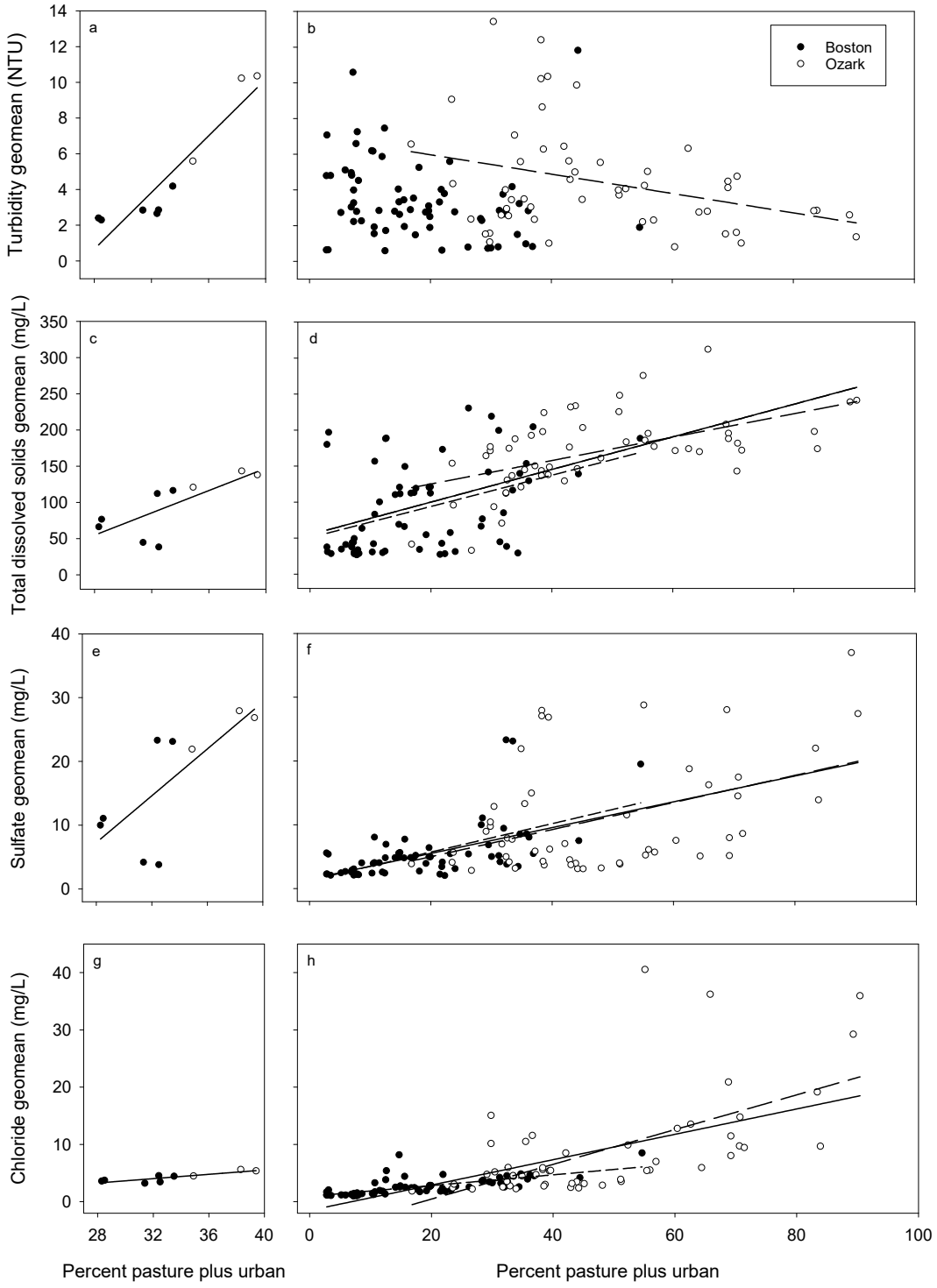

Figure 3. Geometric mean constituent concentrations versus percent pasture plus urban land use in the drainage area of study sites along the West Fork of the White River (WFWR). Panels show: (a) turbidity in the WFWR; (b) turbidity across all 119 sites; (c) total dissolved solids (TDS) in the WFWR; (d) TDS across all 119 sites; (e) sulfate in the WFWR; (f) sulfate across all 119 sites; (g) chloride in the WFWR; and (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.

mg/L across all sites. Percent pasture plus urban land use explained 46, 37, and 48% of the variability in geometric mean chloride concentrations in the entire dataset, the Ozark Highlands, and Boston Mountains, respectively ($p < 0.01$; Figure 3h). The central tendency of the geometric means also differed significantly among ecoregions, where average geometric mean concentrations were 8.9 and 2.7 mg/L in the Ozark Highlands and Boston Mountains, respectively ($p < 0.01$). The variability in geometric mean 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 (28-39%). 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 1-8%; Bolstad and Swank 1997). The land use change in the WFWR watershed could be influencing turbidity in the water column, although there may be other factors driving this change.

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 more strongly influenced turbidity in those studies, as well as in the WFWR. 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 support ecoregion specific criteria, because geometric mean 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 2011). 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 concentrations (data not shown). The nutrient supply in the WFWR is relatively low, even at the most impacted site downstream (average soluble reactive phosphorus 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.

The change in turbidity levels along the WFWR coincides with changes in the dominant riparian soils. Cotton and Haggard (2011) showed that riparian soils change 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 (Cotton and Haggard 2011). Thus, the increased turbidity might be natural due to the change 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 3a and 3b (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 information presented in this paper also suggests that the greater turbidity levels at the downstream sites, as well as across Ozark Highlands sites, might be driven by natural sources (e.g., riparian soil types). This leaves the question, is a limit of 10 NTU appropriate for all sites in the Ozark Highlands? Regulatory agencies should 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 anthropogenic sources of ions, particularly sulfate and chloride, 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 sulfate and chloride concentrations during base flow than primarily forested streams (Fitpatrick et al. 2007). For example, Wright et al. (2011) calculated mean sulfate and chloride concentrations in urban streams (30-70% urban land use) at 13 and 90 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 sulfate and chloride concentrations 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 from Site 5 to 4, where Site 4 is approximately 3.2 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 3b, and includes the abrupt change 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. The ecoregion boundary lies approximately 1.1 km downstream (north) of Site 3b, outside the view of the quadrangle shown in Figure 4. 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 change 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 along the State-defined ecoregion boundary in 2018. Now only the downstream portion is listed as impaired for TDS and sulfate, while the upstream portion is still listed for sulfate (ADEQ 2018). However, the segment divide occurs just downstream of Site 3b, which is approximately 9 km downstream from the change in underlying geology along the river corridor. This malalignment between the defined ecoregion boundary and the true underlying geology is likely due to insufficient data resolution when the boundaries were determined.

A sulfate limit of around 20 mg/L might be appropriate if the intent of the WQS is to preserve natural background conditions in the upstream reaches of 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 change we see in underlying geology, where high sulfate materials like limestone and shale dominate. If the divide is redrawn 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

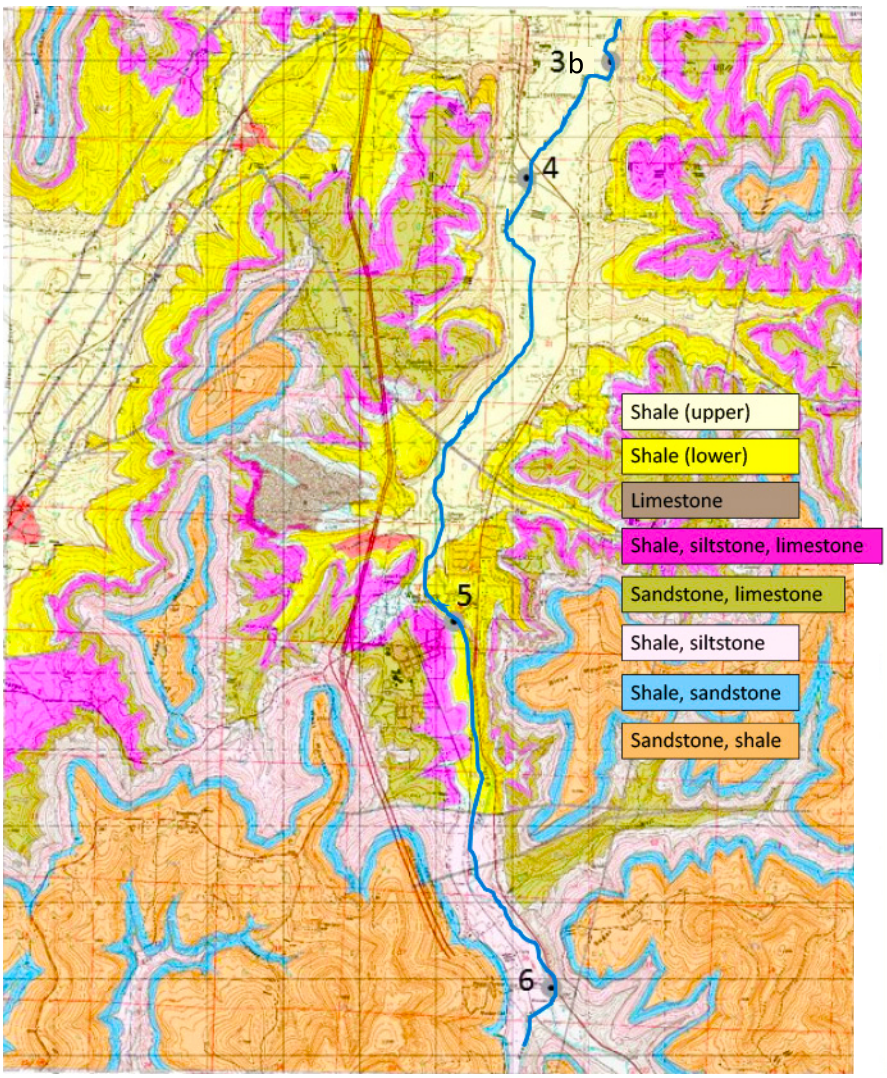

Figure 4. Map of the bedrock geology of the West Fork quadrangle, adapted from King et al. (2002). The blue line represents the West Fork White River (WFWR), which flows from south to north. The dots with numbers show sampling sites and the ecoregion divide is approximately 1.1 km downstream (north) of Site 3b.

Mountains, particularly when groundwater contribution is greater (e.g., during base flow).

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 designated uses, and thus is the basis of the WQS in the WFWR (personal communication, Nathan Wentz, ADEQ). 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 geometric mean 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, 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 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 changes 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 change 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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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.

Designated Use	Impact	-------- Literature Thresholds -------- 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	APCEC 2015; USEPA 2018b
Industrial	Salinity	1000	500	-	Driscoll et al. 2002
Poultry	Flushing; Toxicity	-	200	150	Austin et al. 2016a
Cattle	Laxative; Toxicity	1000-2500	500	1500	Austin et al. 2016b
Swine	Laxative; Toxicity	3000	1000	250	Austin et al. 2016b
Irrigation	Salinity	-	300	142	Austin et al. 2017

*Range is for protection of the most sensitive species.

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