Received: 13 August 2018 | Returned for Revision: 24 September 2018 | Accepted: 20 December 2018

Environmental Management

Multiple Approaches to Surface Water Quality Assessment Provide Insight for Small Streams Experiencing Oil and Natural Gas Development

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ABSTRACT

Historic, current, and future oil and natural gas development can affect water quality in streams flowing through developed areas. We compared small stream drainages in a semiarid landscape with varying amounts of disturbance from oil and natural gas development to examine potential effects of this development on surface water quality. We used physical, chemical, and biological approaches to assess water quality and found several potential avenues of degradation. Surface disturbance likely contributed to elevated suspended sediment concentrations and spill history likely led to elevated stream polycyclic aromatic hydrocarbon concentrations. In combination, these environmental stressors could explain the loss of aquatic macroinvertebrate taxon at sites highly affected by oil and natural gas development. Our results provide insight into advantages and disadvantages of approaches for assessing surface water quality in areas affected by oil and natural gas development. *Integr Environ Assess Manag* 2019;00:000–000. © 2019 SETAC

Keywords: Surface disturbance Sediment Hydrocarbons Macroinvertebrates Water quality

INTRODUCTION

Maintaining and improving surface water quality is important for human and environmental health. In the United States, more than 46% of evaluated streams have been characterized as having poor biological condition (USEPA 2016). Various types of land use have been closely linked to changes in water quality on the basis of their proportional abundance and configuration on the landscape (Allan et al. 1997). Oil and natural gas development (ONGD) has been shown to lead to habitat fragmentation, vegetation conversion, and soil loss (Pierre et al. 2015, 2017; Wolaver et al. 2018).

The rapid expansion of ONGD poses a risk to surface water quality (Entrekin et al. 2011; Burton et al. 2014) and biota (Brittingham et al. 2014; Baker et al. 2018). Several avenues exist through which ONGD can lead to surface water contamination (Figure 1; Entrekin et al. 2011). Point source pollution can occur from spills or leaks associated with the drilling and waste treatment and handling processes (Maloney et al. 2017). In addition, degraded surface water quality can result from nonpoint source pollution associated with infrastructure development. Well pad, pipeline, road, and facility construction can lead to soil erosion and elevated suspended sediment concentrations (Olmstead et al. 2013; Pierre et al. 2015). The use of water in the drilling process can reduce surface water discharge, and low discharge can exacerbate contaminant loads (Whitehead et al. 2009). Quantifying and determining the sources of water quality degradation within areas affected by ONGD has proven difficult and thus requires targeted assessment (Vengosh et al. 2014). The use of a multifaceted approach to study land use effects on surface water quality can be helpful in determining potential pathways of degradation and thus in defining the sources.

Multiple approaches are available for assessing surface water quality within areas affected by ONGD (Figure 1). Physical metrics such as suspended sediment are an affordable way to potentially understand the spatial and temporal mobilization of sediment and associated compounds (Conaway et al. 2013). "Grab" or 1-time samples are commonly used for water chemistry analysis of major ion and trace metal concentrations, which can indicate produced water infiltration (Brantley et al. 2014). As a proxy for dissolved ion concentrations, specific

This article includes online-only Supplemental Data.
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Published 3 January 2019 on wileyonlinelibrary.com/journal/ieam.

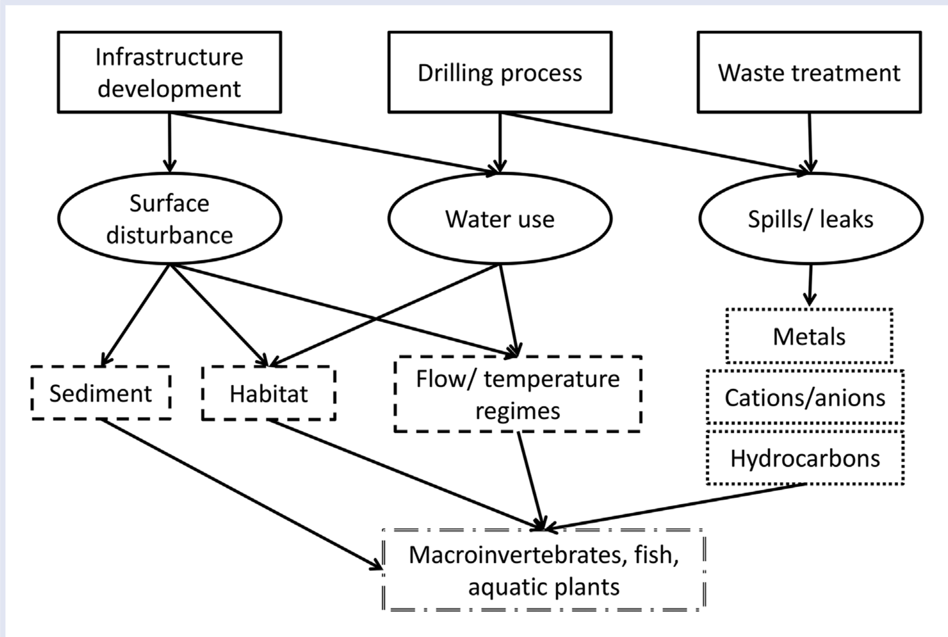

Figure 1. Conceptual figure of major mechanistic pathways through which oil and gas development can affect surface water quality. Potential metrics for assessing effects include physical (dashed line boxes), chemical (dotted lines boxes), and biological (double dash-dotted lined box) metrics.

conductivity measurements can be collected with data loggers, with a spike in conductivity potentially indicating a produced water release. However, major ion, trace metal, and conductivity analyses are rarely a "smoking gun" because alterations of ions that influence conductivity can arise from natural and human sources, including inputs from erosion (Brantley et al. 2014). Oil and gas extraction targets hydrocarbons, so they represent another chemical option for water quality investigations that is less likely to be affected by natural processes. Biological metrics are another useful approach, and many state and federal management agencies monitor benthic macroinvertebrates to evaluate aquatic health impairment. Aquatic macroinvertebrate assemblages integrate over long time periods and multiple potential mechanistic pathways because they are sensitive to both elevated concentrations of compounds (e.g., organics, salts, and trace metals) and more natural stressors such as variation in discharge and temperature (Hilsenhoff 1988; Statzner and Bêche 2010).

Our goals were to 1) assess surface water quality using physical, chemical, and biological metrics in 3 small drainages with varying levels of ONGD activities and 2) evaluate the advantages and disadvantages of the approaches. We hypothesized that sites experiencing greater ONGD would have physical, chemical, and biological metrics reflective of degraded surface water quality. Due to an accidental pipeline release of crude oil into Dry Piney Creek (Upper Green River drainage, Wyoming, USA) at the beginning of our study in 2012, we could relate some metrics to a known contamination event. Where possible we compared our results to earlier monitoring by Wyoming Department of Environmental Quality (WDEQ; Hargett 2003). The present research will provide baseline data prior to proposed redevelopment within the study area (the LaBarge infill project: 838 new wells [BLM 2010]) and can inform decision making and monitoring as regional and national ONGD expands.

METHODS

Study area

Our study area encompasses 4 small streams: Black Canyon, Fogarty, South Beaver, and Dry Piney creeks, in the Upper Green River drainage (Figure 2). South Beaver Creek flows into South Piney Creek before entering the Green River at Big Piney, Wyoming. Fogarty Creek is a tributary to Dry Piney Creek that flows directly into the Green River, 14 km south of Big Piney. Black Canyon Creek is also a tributary of Dry Piney Creek and flows into Dry Piney Creek, 5.6 km upstream of the confluence with Fogarty Creek.

The streams originate from small springs, approximately 2450 m in elevation. Stream discharge is snowmelt dominated and some streams may dry in late summer due to limited rainfall. The streams provide hydrologic support to a narrow corridor of riparian vegetation which is surrounded by drought-tolerant, upland vegetation. The riparian vegetation is primarily willow and sedge with aspen patchily distributed at higher elevations. The upland vegetation is primarily sagebrush steppe with some conifers at higher elevations. The underlying geology in the area is 2 different types of Tertiary Wasatch Formation rock, with a series of north–south faults made out of older rocks.

The LaBarge Oil and Gas Field overlaps Dry Piney, Fogarty, and Black Canyon creeks with the confluence of Fogarty and Dry Piney creeks being the heart of development in the study area. South Beaver Creek is comparable ecologically (vegetation and wildlife) and geologically (valley floor, elevation, surficial geology, and stream geomorphology) to

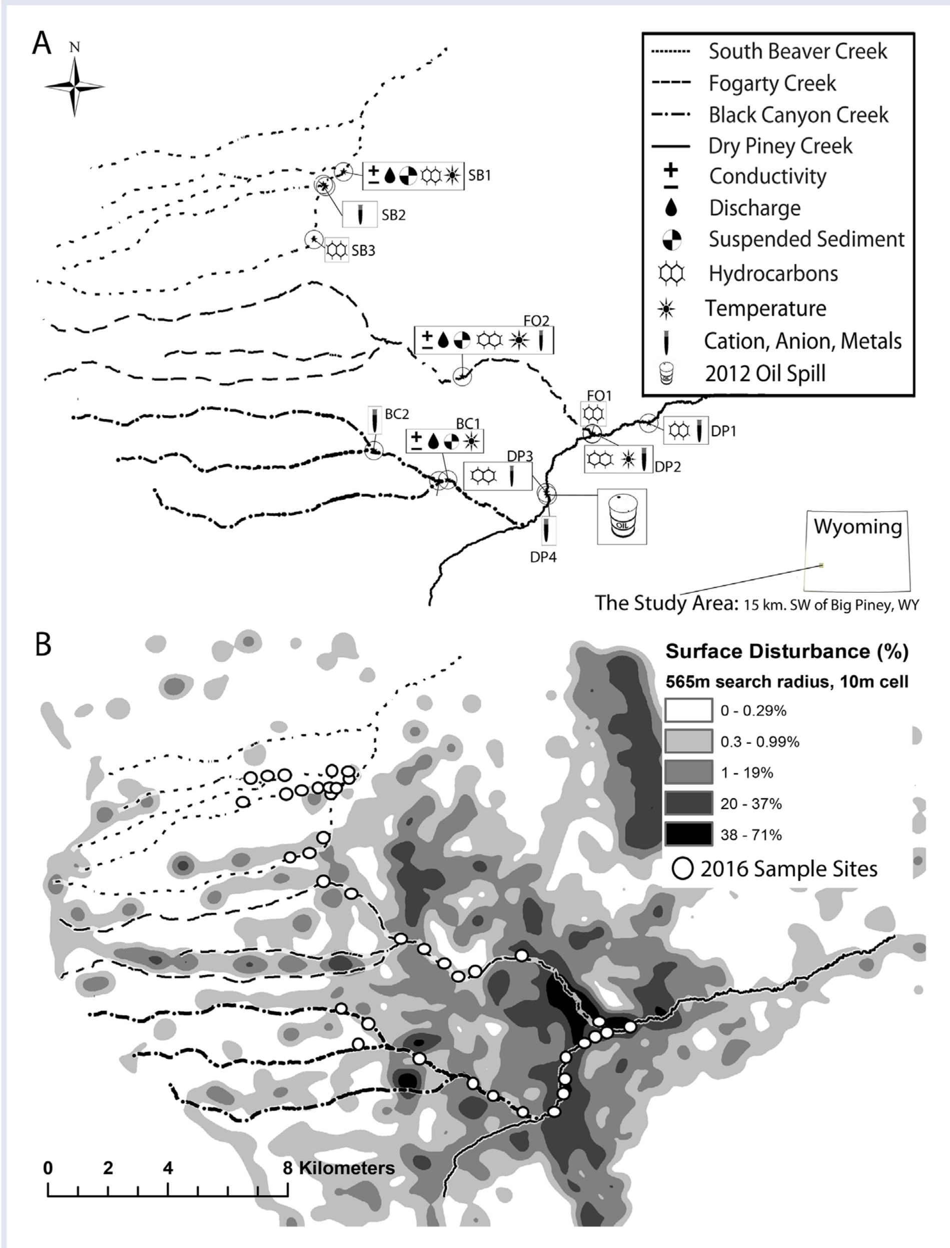

Figure 2. Location of sampling sites and type of data collected at each site (A); the 2016 sites for suspended sediment and macroinvertebrates overlain by a kernel density distribution of surface disturbance (B). Streams flow west to east.

Dry Piney, Black Canyon, and Fogarty creeks, and occurs just north of the LaBarge Oil and Gas Field. The predominant watershed disturbance in the study area is ONGD. There is also cattle grazing, but all of the study area is 1 grazing allotment so all sites receive similar cattle numbers. There is some seasonal variation in grazing as cattle are moved up in elevation as the season progresses to track forage production. There is no other agricultural or urban, suburban, or rural development in the area. Historically, there were a few homesteads, but these have been abandoned and their access roads repurposed for ONGD.

Energy exploration in the region dates initially to the early 1900s. Stream contamination from crude oil and flowback water, via collapse of containment ponds, and pipeline and well failures have been recorded since the 1970s (BLM et al. 1983; Hargett 2003). The most recent spill occurred on 29 March 2012, when 1 to 1.5 barrels (42 gallons/barrel) of crude oil from a pipeline rupture flowed into Dry Piney Creek and approximately 2.5 miles downstream (EOG 2012). This spill occurred right at the beginning of our study so study sites below the spill were included for major ion, trace metal, and polycyclic aromatic hydrocarbon (PAH) sampling. We found no record of current or historic contaminant discharges from ONGD in the South Beaver Creek drainage.

These streams provide an opportunity to evaluate surface water quality in streams potentially altered by long-term ONGD. We sampled multiple sites across these 4 streams although not all metrics were collected at all sites

 DOI: 10.1002/ieam.4118

(Appendix 1). We selected discharge, temperature, conductivity, and suspended sediment sites so there was 1 site in each drainage at comparable elevations (Figure 2). Major ion, trace metal, and PAH sites were chosen opportunistically, taking into account the 2012 oil spill. In 2016, we sampled macroinvertebrate and suspended sediments from 40 sites, randomly selected from evenly distributed locations every 500 m along the stream network.

We used surface disturbance to quantify ONGD intensity for each site. We calculated percent surface disturbance (%SD) at the catchment scale by quantifying the percent of the landscape altered by ONGD infrastructure such as well pads, roads, facilities, pipelines, and water holding ponds. We delineated catchment polygons for each study site using the ArcGIS Watershed toolbox (ESRI 2011). The workflow included using the Fill tool to eliminate depressions without outflow, snapping sampling locations to the cells of highest value within a 10-m radius on a flow accumulation model, and using the Watershed tool to delineate subcatchment boundaries (Girard and Walters 2018). Subcatchments were converted to polygons and merged so that they included the full catchment area above the site. ONG well data originated from the Wyoming Oil and Gas Conservation Commission GIS well layer (2013; http://wogccms.state.wy.us/flexviewers/unitmap/). We used a US Geological Survey well pad scar data layer (Garman and McBeth 2014) and hand digitization from 2013 Arc GIS Basemap imagery to quantify surface disturbance for all infrastructure. We combined well pad scar with polygons of facility disturbance, and then added linear road and pipeline digitization after buffering them by the average disturbance widths found within the study area. Improved roads that were created by grading were buffered on each side by 5 m, whereas roads that were created by vehicle wear, also known as "2-track roads," were buffered by 1 m, and pipelines by 7.5 m. We also calculated well density for each catchment and observed strong correlations between %SD and well density ($r = 0.92$).

Physical metrics

Temperature and discharge. We measured temperature and discharge in 4 streams: South Beaver (site SB1), Black Canyon (BC1), Fogarty (FO2), and Dry Piney (DP2; discharge only available for 2014–2016) from May to September from 2012 to 2016 (Figure 2). South Beaver, Black Canyon, and Fogarty sites were at a similar elevation (2291–2327 m). Discharge and temperature sites consisted of a fixed pressure transducer (Onset HOBO Water Level Loggers) placed in a stream section with a straight, rectangular channel. We used the cross-sectional method to regularly measure discharge at each site with a Marsh-McBirney Flowmate-Model 2000 (Buchanan and Somers 1969). Continuous discharge was estimated by constructing a discharge rating curve using measured discharge and associated pressure transducer data. Empirical temperature data were compared to modeled stream temperatures generated by the US Forest Service for the western United States at a 1-km resolution (http://www.fs.fed.us/rm/boise/AWAE/projects/NorWeST.html) (Isaak et al. 2016). We compared modeled historical (1993–2011) mean August temperatures to our measured mean August temperature values.

Suspended sediment. We collected suspended sediment samples at South Beaver (SB1), Black Canyon (BC1), and Fogarty (FO2) creeks approximately weekly in 2012 and 2013 using a depth integrated isokinetic sampler (DH-48). In 2016 we collected 40 samples across the study area to get better spatial representation of suspended sediment concentration variation. For all years, we filtered each sample with 1-μm fiberglass, ashed filters. We then weighed the filtrate, which we converted to a water volume, and dried filters in a desiccating oven for 4 h at 60 °C. We calculated each sample's suspended sediment weight by subtracting the original filter weight from the weight of the dried filter containing the suspended solids and dividing this weight of total suspended solids (grams) by the volume of water collected in the water sample (liters).

For 2012 and 2013 samples, we compared suspended sediment concentrations among sites using a repeated measures analysis of variance (function "aov") with sediment sampling events as the repeated measure. We lognormal transformed all suspended sediment concentration data to meet the assumption of normality, tested for equal variance, and completed post-hoc analyses using a Tukey HSD test. For 2016 samples, we used a linear mixed-effects model to evaluate the relationship between suspended sediments and %SD. We used catchment area and drainage as separate random effects in the model.

Chemical metrics

Major ions and trace metals. We collected 7 grab samples for major ion and trace metal analyses on 20 August 2012 (Figure 2). We took 1 sample each from a site near our discharge sites: SB2, BC2, and FO2. We took an additional 4 samples along Dry Piney Creek (DP14) because we were interested in the potential effects of the March 2012 oil spill. These samples included sites 100 m above (DP4) and below (DP3) where crude oil from the pipeline rupture entered the stream, and 2 sites further downstream (DP1 and DP2; Figure 2). We placed samples on ice until delivery at the Wyoming Department of Agriculture Analytical Services Laboratory, Laramie, Wyoming. Cation concentrations were determined with an inductively coupled plasma mass spectrometer (ICP-MS), by USEPA method 200.8. Anions were determined with ion chromatography by USEPA method 300.1 (Pfaff and Hautman 1997). At each discharge site (SB1, BC1, FO2, DP2 [only 2014–2016]) we also placed a conductivity logger (Onset, HOBO Fresh Water Conductivity Data Logger) from 2012 to 2016.

Polycyclic aromatic hydrocarbons. We measured PAH concentrations with fixed semipermeable membrane devices (SPMDs). These mimic biological tissues and provide information on the bioavailability of trace organics that could potentially harm aquatic biota (Huckins et al. 1990). We deployed SPMDs at 2 to 3 sites in each stream: Dry Piney (DP1, DP2, DP3), Fogarty (FO1, FO2), and South Beaver Creeks (SB1, SB3) from 28 May to 26 June 2013 (Figure 2). The 5 samplers per stream were combined to create 1 composite analytical sample per stream. To diminish potential SPMD contamination, Columbia Environmental Research Center protocols were followed (Seiders et al. 2012), including the use of blanks and clean handling and storage techniques. SPMDs were placed in pools that had consistent, unidirectional velocities and a low likelihood of dewatering.

Biological metrics

We sampled forty 150 m sites in August 2016 to evaluate the potential effects of ONGD on benthic macroinvertebrate assemblages (Figure 2). We collected benthic macroinvertebrates at 6 random locations in each site by disturbing the substrate within a 15.25 cm diameter Hess sampler (335-μm mesh) for approximately 25 s (240 samples). Sample locations within a site were selected using a random number generator in which every stream meter (0–150 m) had an equal chance of being initially selected. All sample locations were required to have at least 10 m between each location; therefore, if sample locations were within 10 m of each other, an additional random number was generated until all locations met the 10 m requirement.

Macroinvertebrate samples were preserved in 70% ethanol and transported back to the laboratory at the University of Wyoming for further processing. All macroinvertebrates were separated from all organic and inorganic matter, identified to genus where possible, enumerated, and measured to the nearest 1 mm. In the case of Chironomidae (Diptera), individuals were identified as being nonpredaceous (non-Tanypodinae) or predaceous (Tanypodinae). In addition, all individuals of Nemouridae and Chloroperlidae were grouped by family. Macroinvertebrates were grouped into functional feeding guilds (FFGs; i.e., shredders, collector-gatherers, collector-filterers, scrapers, and predators) based on Merritt et al. (2008).

We calculated and compared a series of macroinvertebrate metrics across the 40 sites. Macroinvertebrate diversity; taxon richness; Ephemeroptera, Plecoptera, and Trichoptera (EPT) taxon richness; percentage EPT; and density and biomass of all benthic macroinvertebrates and each FFG were calculated. We used Shannon's diversity index to calculate benthic macroinvertebrate diversity. Taxon and EPT richness were measured as the number of unique macroinvertebrate taxa collected at each site. Densities were calculated as the number per square meter for each corresponding response variable. We estimated macroinvertebrate biomass of all benthic macroinvertebrates and each FFG using previously established length-to-mass relationships (Benke et al. 1999).

We used linear mixed-effects models to evaluate the relationships between benthic macroinvertebrate metrics and %SD. Where appropriate, data transformations were applied to meet the assumptions of normality and homogeneity of the variance (e.g., percent data logit-transformed and other data log10-transformed). To account for spatial autocorrelation and multiple samples within a site, we included sites nested within drainage and catchment area (km^2) as separate random effects in all models (Zuur and Ieno 2016). For each model, we considered parameters insignificant if the predictor's confidence intervals overlapped zero and at an $\alpha > 0.05$ (Nakagawa and Schielzeth 2013).

We used Threshold Indicator Taxa Analysis (TITAN; Baker and King 2010) to identify thresholds along the %SD gradient that correspond with distinct macroinvertebrate assemblages. We performed TITAN with the TITAN2 package (Baker et al. 2015) with untransformed taxa abundances for taxa with greater than 3 occurrences. All analyses were performed in Program R (R Core Team 2018).

RESULTS

Physical metrics

Catchment %SD was lower for South Beaver Creek (SB1: 2.3%, SB2: 3.5%, SB3: 3.9%) and Black Canyon Creek (BC1: 2.7%, BC2: 2.1%) sites, and greater for Fogarty Creek (FO1: 9.2%, FO2: 6.1%) and Dry Piney Creek (DP1: 8.4%, DP2: 7.7%, DP3: 6.9%, DP4: 6.6%) sites (Appendix 1).

South Beaver and Dry Piney creeks had the greatest average discharge and variation in discharge in most years (Figure 3A), with 2012 and 2013 having the lowest discharge at all sites relative to other years. Daily mean water temperature was, on average, greatest at Dry Piney Creek in all years (Figure 3B). South Beaver Creek had the lowest daily mean temperature in most years, being relatively similar to Black Canyon and Fogarty creeks during the drier periods in 2012 and 2013 (Figure 3B). Modeled mean August temperatures were consistently higher than average August temperatures experienced over the study period, except for Dry Piney Creek, which was warmer than modeled (Appendix 2).

Suspended sediment concentrations were highly variable between 2012 and 2013, among sites, and through time (Appendix 3). There were statistically significant differences ($df = 2$, f-value $= 8.3$, $p = 0.001$) among sites with post-hoc analysis finding that Black Canyon and Fogarty creeks' suspended sediment concentrations were not significantly different but were significantly greater than South Beaver Creek's (Appendix 3). During baseflow conditions in August 2016, suspended sediment concentrations were positively related to %SD (Figure 4).

Chemical metrics

Specific conductivity was variable across streams and years. On average, Black Canyon and Dry Piney creeks had the greatest specific conductivity (Figure 3C) in all years. Specific conductivity was greatest in all streams in 2012 and 2013, which corresponded with years of lowest discharge (i.e., 2012 and 2013).

Major ion and trace metal concentrations differed among sites and streams; however, none of the metrics tested exceeded concentrations deemed unsafe for human and livestock use (Table 1). Of the 45 metrics evaluated, 17 were

 DOI: 10.1002/ieam.4118

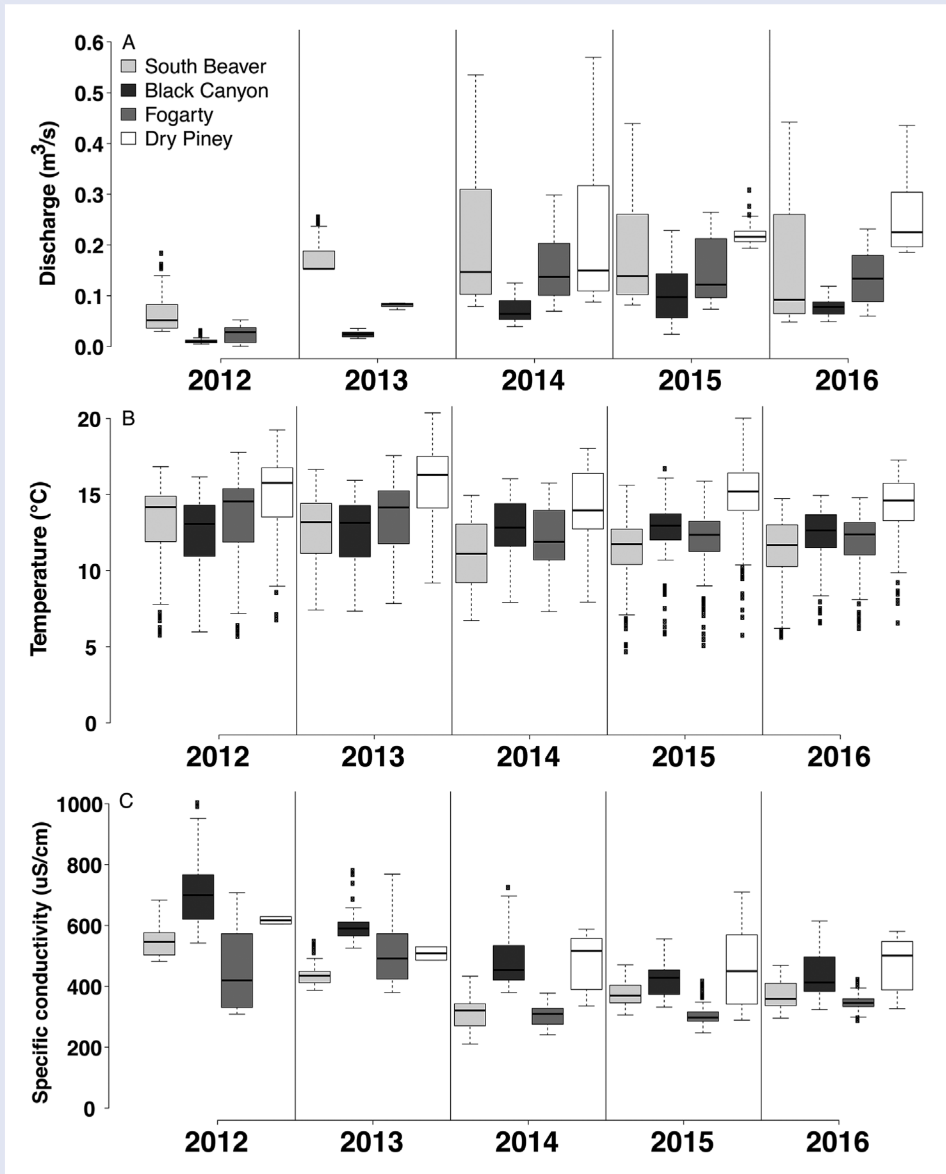

Figure 3. Boxplots showing differences in mean daily discharge (A), temperature (B), and conductivity among sites (C) (South Beaver: SB1, Black Canyon: BC2, Fogarty: FO2, and Dry Piney: DP2 [Upper Green River drainage, Wyoming, USA]) between 2012 and 2016. Data are unavailable for discharge at Dry Piney in 2012 and 2013. Continuous daily conductivity for Dry Piney in 2012 and 2013 are unavailable; values are based on haphazard in-situ samples taken with a handheld YSI Professional Plus meter (YSI Inc.). Sites are ordered from least to greatest percent surface disturbance (%SD).

below detection limits at all sites. Many of these metrics had the greatest chemical concentrations at DP1, the farthest downstream site (Table 1). The results from ion and trace metal measurements taken 100 m above and below the oil spill location (DP3 and DP4) were nearly identical.

Sample concentrations for 23 of the 33 PAHs investigated were above detection limits. Extracts from SPMDs at Dry Piney Creek had the most PAHs (21 compounds found), and generally, PAH concentrations were greater than in other streams (Table 2). Fogarty Creek and South Beaver Creek samples yielded 17 and 6 PAH compounds, respectively.

Biological metrics

After accounting for catchment area and repeated samples at each site, we found several significant relationships between %SD and our benthic macroinvertebrate metrics. For our focal community metrics, taxon richness, EPT richness, %EPT, and total macroinvertebrate density and biomass were negatively related to %SD (Table 3). Shredder and collector-filterer density and biomass were also negatively related to %SD, as was collector-gatherer density, but not biomass (Table 3).

The maximum sum $z-$ change point identified by TITAN was 4.16 (2.88, 6.03; 5th and 95th percentiles respectively) and the maximum sum $z+$ change point was 6.41 (4.03, 7.04). The broad band of confidence limits and overlap of confidence interval suggest a continuous threshold range, over which species that are generally more strongly associated with the lower end of the gradient are supplanted by those that are generally more strongly

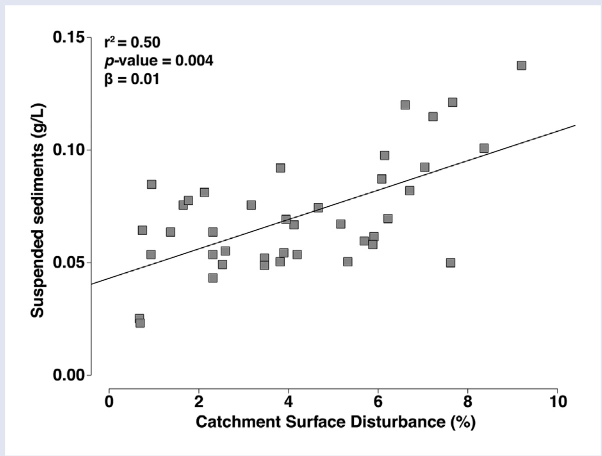

Figure 4. Linear relationship between suspended sediments and percent surface disturbance (%SD) during base flow conditions in August 2016.

associated with the higher side of the gradient (Baker and King 2013). The TITAN analysis identified 13 taxa (27%) that sharply declined in response to increasing %SD and 3 taxa (6%) that sharply increased (Appendix 4).

DISCUSSION

Surface water quality differed among sites. Stream sites in areas with the greatest density of ONGD showed some evidence of physical, chemical, and biotic impairment. These streams had elevated concentrations of PAHs, increased suspended sediment concentrations, and a decreased macroinvertebrate taxon richness. A history of point-source pollution (spills and leaks) and erosion from oil and gas-related surface disturbance are the 2 mechanisms likely contributing to reduced surface water quality in the disturbed streams (Figure 1).

The results of this study are similar to WDEQ monitoring (Hargett 2003), which assessed water quality conditions in Dry Piney Creek, and reported oil deposits in the streambed sediments, elevated total dissolved solids, and fair to poor macroinvertebrate assemblages in the highly developed areas. The WDEQ reports indicated that ONGD could be contributing to poor water quality, but the most recent report states that results are inconclusive and further investigation is required (Thorp 2016). Our research expands on that carried out by WDEQ with increased frequency of monitoring and additional methods such as measurements of bioavailable fractions of PAHs. The use of multiple approaches and the consistent direction of results allow us to conclude that ONGD in this area has some adverse effects on surface water quality.

The present study supports the finding that spills and leaks are an important mechanism affecting surface water quality. Our results indicate that petroleum contamination is not limited to the streambed in Dry Piney Creek, as documented by WDEQ (Hargett 2003), but that PAHs infiltrate the surface water. Of the 23 PAHs found in the study streams, 9 were USEPA priority pollutants, but all were below USEPA drinking water standards (USEPA 2012) and standards for the protection of aquatic life (USEPA 1986). Because of the proximity to ONGD, we suspect that ONGD is the likely cause of elevated PAHs. Although variation in geology could account for some variation in water quality, the presence and elevation in concentrations of USEPA priority pollutant PAHs is less likely. The higher number and levels of PAHs in Dry Piney Creek are likely in part the result of the 2012 pipeline rupture that spilled crude oil into Dry Piney Creek (EOG 2012). Fogarty Creek, which was not affected by the 2012 oil spill, also had a substantial number of PAH species present at generally greater concentrations than South Beaver Creek. This PAH signature is likely a legacy of historical spills in Fogarty Creek, which have included pit failures, storage tank leaks, and pipeline ruptures (BLM et al. 1983; Hargett 2003). During high flow events, PAHs may also be contained in streambed sediments and mobilized. In PAH-polluted rivers, sediment mobilization and turbidity can be associated with greater PAH concentrations (Conaway et al. 2013).

We also found support for surface disturbance as a mechanism driving shifts in water quality. Surface disturbance is a well-known avenue of aquatic degradation (Bern et al. 2015; Baker et al. 2018), and %SD was correlated with greater suspended sediment concentrations and decreases in macroinvertebrate taxon richness and several functional feeding groups' density and biomass. The source of suspended sediment is likely physical disturbance in the active stream channel and in the adjacent uplands (i.e., streambed and bank incision, digging in the creek, channelizing overland flow, poor culvert placement, and livestock trampling). The importance of surface disturbance as a mechanism is likely related to the erodibility of the underlying geologic formation. In our study area, the underlying rock formation (Tertiary Wasatch Formation) is easily erodible and has a high concentration of dissolved solids (Mason and Miller 2005).

We did not find support for water use being a major mechanism that drives shifts in water quality. Although it is known that ONGD can alter natural hydrology due to increased road networks, increased impervious surfaces, and water use (Forman and Alexander 1998), much of our discharge variation was related to variation in winter snowfall and corresponding melt patterns. Without historical data, it is difficult to determine what differences in discharge among sites are related to ONGD.

Comparing approaches

We used a variety of common approaches to assess surface water quality, including chemical, physical, and biological metrics. We discuss advantages and disadvantages of these and other approaches and suggest best uses in the remainder of this section and in Table 4.

Physical measures of surface water quality often focus on suspended sediment, the most common stream impairment according to the USEPA, because it can provide a comparable metric among streams, is affordable, provides good insight into watershed condition, and can be combined with discharge data (Newcombe and Macdonald 1991). We found strong relationships between %SD and suspended sediment with spatially focused sampling, but the temporally focused sampling revealed much greater variation. Mean suspended sediment concentrations at our sites were comparable to the 2003 WDEQ study (0.032 and 0.043 g/L; Hargett 2003); however, our maximum suspended sediment concentrations (Appendix 3) were an order of magnitude above WDEQ measurements, illustrating the importance of repeated measurements to characterize the full range of variation. The other physical metrics we considered (temperature and discharge) also had high natural variability and were hard to directly link to ONGD. Comparing empirical and modeled temperatures is one approach for determining discrepancies that could indicate potential degradation. For 3 of our sites, measured

Table 1. Major ion and trace metal concentrations for 20 August 2012 water samples[abc]

Metric	Concentrations in Green River creeks, Wyoming, USA						
	Black Canyon 3	South Beaver 2	Dry Piney 4	Dry Piney 3	Dry Piney 2	Dry Piney 1	Fogarty 1
pH	8.5	8.4	8.3	8.4	9.2	8.6	8.4
Conductance (μS/cm)	480	420	580	580	500	750	480
TDS (mg/L)	270	230	320	330	280	420	260
Alkalinity ($CaCO_3$)	260	230	270	270	220	260	240
Hardness (mg/L)	290	250	330	330	280	340	260
Bicarbonate (mg/L)	303	270	320	330	190	290	280
Carbonate (mg/L)	9.1	4.0	1.7	2.6	38.0	12.0	4.7
Calcium (mg/L)	50.0	56.0	49.0	50.0	18.0	36.0	42.0
Magnesium (mg/L)	40.0	27.0	50.0	50.0	57.0	60.0	37.0
Sulfate (mg/L)	7.1	6.3	36.0	36.0	42.0	54.0	8.0
Chloride (mg/L)	3.5	2.3	13.0	14.0	17.0	65.0	15.0
Sodium (mg/L)	5.7	3.0	13.0	13.0	16.0	50.0	15.0
Silica (mg/L)	8.2	6.7	7.4	7.3	2.7	4.2	4.9
Silicon (mg/L)	3.9	3.1	3.4	3.4	1.2	2.0	2.3
Potassium (mg/L)	2.1	1.0	1.9	1.9	1.4	1.6	1.3
Fluoride (mg/L)	0.2	0.1	0.3	0.3	0.2	0.2	0.2
Barium (mg/L)	0.263	0.138	0.147	0.150	0.061	0.134	0.237
Strontium (mg/L)	0.117	0.112	0.162	0.166	0.125	0.204	0.211
Boron (mg/L)	0.031	0.020	0.043	0.043	0.032	0.075	0.036
Lithium (mg/L)	0.014	0.005	0.017	0.017	0.020	0.028	0.017
Vanadium (mg/L)	0.009	0.001	0.005	0.004	0.005	0.003	0.002
Aluminum (mg/L)	0.002	0.003	0.002	0.002	0.004	0.003	0.002
Arsenic (mg/L)	0.003	0.002	0.002	0.002	0.002	0.002	0.001
Uranium (mg/L)	0.001	<0.001	0.003	0.003	0.003	0.004	0.001
Molybdenum (mg/L)	0.001	<0.001	0.002	<0.001	0.003	0.003	<0.001
Zinc (mg/L)	<0.001	0.001	0.001	<0.001	<0.001	<0.001	<0.001
Copper (mg/L)	<0.001	<0.001	0.001	0.001	0.001	0.001	<0.001
Selenium (mg/L)	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001

TDS = Total dissolved solids.
[a] All concentrations preceded by "<" indicate values below detection limit.
[b] We also tested for acenaphthylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c*,*d*]pyrene, dibenz[*a*,*h*]anthracene, benzo[*g*,*h*,*i*]perylene, benzo[*b*]thiophene, 9-methylanthracene, and benzo[e]pyrene, but these were below detection limits for all sites.
[c] Sites are ordered from least to greatest percent surface disturbance (%SD).

Table 2. Polycyclic aromatic hydrocarbon concentrations from 1-month semipermeable membrane device exposures[a,b]

	Concentrations in Upper Green River creeks, Wyoming, USA (ngL^{-1})		
Polycyclic aromatic hydrocarbons	South Beaver	Fogarty	Dry Piney
Naphthalene	<0.14	1	1.9
Acenaphthene	<0.002	<0.002	0.15
Fluorene	<0.002	0.12	0.15
Phenanthrene	0.094	0.25	1.6
Anthracene	<0.002	<0.002	0.38
Fluoranthene	0.051	0.064	0.34
Pyrene	0.033	0.044	0.32
Benz[*a*]anthracene	<0.002	<0.002	0.022
Chrysene	<0.002	0.084	0.21
2-methylnaphthalene	0.063	1.8	1.5
1-methylnaphthalene	<0.002	1.1	1.3
Biphenyl	<0.002	0.44	0.3
1-ethylnaphthalene	<0.002	0.1	0.36
1,2-dimethylnaphthalene	<0.002	0.14	<0.002
4-methylbiphenyl	0.9	1.1	1.8
2,3,5-trimethylnaphthalene	<0.002	0.21	5.5
1-methylfluorene	<0.002	0.14	3.4
Dibenzothiophene	<0.002	0.071	0.42
2-methylphenanthrene	<0.002	0.09	1.3
3,6-dimethylphenanthrene	<0.002	0.027	0.98
2-methylfluoranthene	<0.002	<0.002	0.083
Benzo[*b*]naphtho[2,1-*d*]thiophene	<0.002	<0.002	0.084
Perylene	0.058	<0.002	<0.002
Site total PAH concentration	1.20[c]	6.78[c]	22.10[c]
Average PAH concentration	0.17[c]	0.40[c]	1.05[c]
Number of PAHs	6[c]	17[c]	21[c]

[a] All concentrations preceded by a "<" indicate values below detection limit.
[b] We also tested for acenaphthylene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c*,*d*]pyrene, dibenz[*a*,*h*]anthracene, benzo[*g*,*h*,*i*]perylene, benzo[*b*]thiophene, 9-methylanthracene, and benzo[*e*]pyrene, but these were below detection limits for all sites.
[c] Summary values.

temperatures were below modeled, but Dry Piney Creek temperatures were above (Appendix 2). Dry Piney Creek experiences the greatest amount of ONGD, including loss of riparian habitat, which could be contributing to increased temperatures.

Surface water quality testing often involves chemical analysis, especially of major ions and trace metals. Although PAHs are useful and logical, they often are avoided because they involve more expensive measurements (Lebo et al. 1992). We originally focused on major ion and trace metal sampling and were unable to detect the 2012 oil spill, with virtually identical results above and below the spill location. In contrast, PAHs captured the spill event a year later and provided evidence for historical spills. Major ions and trace metals would likely have been more appropriate for a spill of produced water, highlighting that knowledge of potential contaminants is a better guide for method selection than are simplicity and cost. In addition, major ions and trace metals tend to be collected with grab samples so are just representative of conditions at the time the sample was taken, whereas the SPMDs can be deployed for longer durations, allowing them to integrate over a longer time

 DOI: 10.1002/ieam.4118

Table 3. Results of linear mixed-effects models evaluating the relationships between benthic macroinvertebrate metrics and %SD

Response metric	β	SE	*t*-value	*p*-value	CI	R^2
Diversity	–0.07	0.13	–0.59	0.50	–0.36, 0.16	0.25
Taxon richness[a]	–0.14	0.04	–3.61	<0.001	–0.22, –0.07	0.18
EPT richness[a]	–2.56	0.80	–3.21	0.001	–4.11, –0.92	0.34
Percent EPT[a]	–0.70	0.35	–1.99	0.04	–1.39, –0.01	0.12
Total invertebrate density[a]	–0.29	0.11	–2.63	0.009	–0.54, –0.10	0.25
Shredder density[a]	–1.59	0.28	–5.61	<0.0001	–2.14, –1.03	0.38
Collector-filterer density[a]	–0.50	0.24	–2.11	0.04	–0.96, –0.04	0.17
Collector-gatherer density[a]	–0.30	0.12	–2.60	0.009	–0.53, –0.06	0.29
Scraper density	–0.38	0.31	–1.23	0.22	–0.98, 0.22	0.39
Predator density	–0.14	0.17	–0.83	0.41	–0.61, 0.17	0.30
Total invertebrate biomass[a]	–0.26	0.12	–2.16	0.03	–0.49, –0.02	0.16
Shredder biomass[a]	–1.50	0.31	–4.90	<0.0001	–2.06, –0.68	0.34
Collector-filterer biomass[a]	–0.96	0.28	–3.38	<0.001	–1.51, –0.40	0.22
Collector-gatherer biomass	–0.14	0.16	–0.86	0.39	–0.47, 0.18	0.28
Scraper biomass	–0.03	0.04	–0.79	0.43	–0.11, 0.04	0.34
Predator biomass	0.16	0.28	0.55	0.58	–0.61, 0.67	0.37

%SD = percent surface disturbance; EPT = Ephemeroptera, Plecoptera, and Trichoptera.
[a] Significant relationship.

period. Sampling strategies with broad spatial and temporal extent will improve the chances of capturing unknown water contamination events (Alvarez et al. 2008).

We focused on aquatic macroinvertebrates as our biological metric, but there was also ongoing fish sampling at the sites (Girard and Walters 2018). Aquatic macroinvertebrates are one of the most commonly used ecological endpoints because they are a dominant taxonomic group, they integrate effects of all contributing stressors, and measurements are affordable (Statzner and Bêche 2010). However, given the multiple factors that limit macroinvertebrate communities, it can be difficult to directly relate impaired macroinvertebrate communities to a specific disturbance. In our study, both of our analyses (mixed-effects models, TITAN) supported declines in macroinvertebrate with increasing ONGD. There were strong decreasing trends in 10 of our 16 macroinvertebrate metrics examined across a surface disturbance gradient and no increasing trends. Of the functional feeding groups, shredders, collector-filterers, and collector-gatherers showed declines that could be due to loss of riparian vegetation (shredders) and increased sediment (collectors) associated with ONGD. The TITAN analysis found a substantially greater number of taxon that showed a decreasing trend with increasing %SD; of the taxon showing a decreasing trend, 54% were EPT taxon compared to 33% of the increasing taxon. Although TITAN did identify thresholds in %SD that were associated with compositional changes, TITAN is programmed to identify a threshold regardless of whether a true community-level threshold exists. Given the large confidence intervals of the identified thresholds, it seems that what is occurring in this study area is more gradual compositional shifts across the development gradient (Baker and King 2013).

Ideally, one would be able to have multiple measurements of a large suite of metrics distributed across space and time, but this is not always feasible. Many of our analyses were limited by low sample sizes, which is often the case in surface water quality studies. Follow-up monitoring should focus on more repeated sampling for the major suspected mechanistic pathways. In general, recognizing the potential pathways of surface water quality deterioration is a precursor to successfully collecting baseline and follow-up water quality monitoring data in areas of ONGD. If one is most concerned about spills, then water chemistry and macroinvertebrate data are good candidate approaches (Table 4). For surface disturbance and water use pathways, sediment and discharge, respectively, are good choices. However, suspended sediment concentrations and hydrology can be controlled by land use practices, climate, and geology, so predevelopment data is very important. We had no predevelopment data, and thus we chose similar-sized study streams with an adjacent parallel configuration to decrease the inherent variability derived from watershed morphology or local climate. As natural variation in climate, hydrology, and stream chemistry of the study site increases, so does the need to increase sampling frequency and duration.

Table 4. Comparison of approaches for assessment of water quality

Approach	Strengths	Weaknesses	Best uses
Physical			
Discharge	Important driver in aquatic ecosystems, can strengthen interpretation of other data.	Sampling intensive, high natural variation.	Long-term monitoring
Suspended sediment	Easily sampled, good indicator of watershed health, direct effects on ecology and stream morphology.	High natural variation, influenced by discharge and stochastic events.	Pre- and postdevelopment sampling
Temperature	Easy and inexpensive to monitor continuously.	High natural variation, multiple causal pathways.	Long-term monitoring
Stream and riparian habitat	Established protocols, interpretable data, directly linked to ecological condition.	Multiple causal pathways, effects may take considerable time to be apparent.	Pre- and postdevelopment monitoring
Chemical			
Conductivity	Continuous monitoring feasible, can provide indication of produced water release.	Natural variation exists, most informative if linked with data on known dissolved ions.	Long-term monitoring, pre- and postdevelopment sampling
Major ions	Relatively easy and affordable, establishes baseline chemical composition of water.	Natural variation exists.	Pre- and postdevelopment sampling, postevent sampling
Trace metals	Toxicity is well studied, relatively easy and affordable.	Specific metals are not of concern if they are not present in surficial or producing formations.	Pre- and postdevelopment
Hydrocarbons	Can allow definitive assessment of contamination from petroleum sources, does not occur frequently at surface from natural sources.	Can be complex and expensive to sample, many hydrocarbons have short residence time mixed in waters.	Pre- and postdevelopment sampling, postevent sampling
Biological			
Fish	Management-relevant data, good indicator of ecological function that integrates multiple stressors, long-lived.	Highly mobile, effects may take considerable time to be apparent, multiple causal pathways.	Pre- and postdevelopment sampling
Macroinvertebrates	Diverse group and good indicator of ecological function that integrates multiple stressors, used in regulatory monitoring, results can be compared to regional datasets.	Multiple causal pathways, inconsistent sampling protocols, substantial lab processing time, challenging taxonomy.	Long-term monitoring, pre- and postdevelopment sampling, postevent sampling
Plants and algae	Can be diverse and specialized to certain conditions, pairs well with macroinvertebrate sampling.	Multiple causal pathways, typically requires a taxonomic specialist, substantial lab processing time.	Long-term monitoring, pre- and postdevelopment sampling

CONCLUSIONS

Our research found that stream sites with less ONGD had lower suspended sediment concentrations and higher macroinvertebrate richness and density. In contrast, sites with greater ONGD had more PAHs, elevated suspended sediment concentrations, and lower macroinvertebrate richness, density, and biomass. The consistent direction of effects across multiple metrics supports our hypothesis that ONGD is contributing to surface water quality deterioration in the study area. Our study highlights the benefits of using multiple approaches. Water quality assessment that uses multiple sampling approaches, baseline data, and reference comparisons can help overcome some of the challenges presented by natural variation and potential sources of contamination (Vengosh et al. 2014).

Acknowledgment—We thank private landowners for access, Roger Hopper and David Harper for water quality monitoring guidance, and Travis Schmidt for providing comments that improved the manuscript. Funding for this work was provided by the Wyoming Landscape Conservation Initiative.

Disclaimer—The authors declare no conflicts of interest. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government.

Data Accessibility—Data associated with this project can be found in ScienceBase at https://doi.org/10.5066/P9OF7K9V.

SUPPLEMENTAL DATA

Appendix 1A. List of sites, their locations, percent catchment surface disturbance (%SD), and data collected.

Appendix 1B. Sites sampled in 2016 for suspended sediment and macroinvertebrates.

Appendix 2A. Comparison of August mean temperature (2012–2016) for South Beaver (SB1), Black Canyon (BC1), Fogarty (FO2), and Dry Piney (DP2) creeks (Upper Green River drainage, Wyoming, USA) with modeled historical (1993-2011) mean August temperatures from NorWest (http://www.fs.fed.us/rm/boise/AWAE/projects/NorWeST.html).

Appendix 2B. August mean temperature for South Beaver (SB1), Black Canyon (BC1), Fogarty (FO2), and Dry Piney (DP2) creeks (Upper Green River drainage, Wyoming, USA) broken down by year.

Appendix 3. Temporal changes in suspended sediments for Black Canyon (BC1), Fogarty (FO2), and South Beaver (SB1) creeks (Upper Green River drainage, Wyoming, USA) in 2012 and 2013.

Appendix 4. Significant macroinvertebrate indicator taxa identified by threshold indicator taxa analysis (TITAN) across a gradient in catchment percent surface disturbance. Filled black circles correspond to declining taxa ($z-$) changepoints and open circles correspond to increasing taxa ($z+$) changepoints. Symbols are sized in proportion to the magnitude of their response (z-score) and horizontal lines indicate 5th and 95th percentiles among 500 bootstrap replicates.

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 DOI: 10.1002/ieam.4118