

2018-2019 Smith River Metals Study

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Executive Summary

The Smith River is an important recreational, agricultural, and ecological resource in Montana, with its stunning scenery and renowned trout fishery. Due to its popularity and importance to recreators, it is currently the only river in Montana requiring a floater's permit. From 2015 to 2017, the Montana Department of Environmental Quality (DEQ) and Montana Fish, Wildlife and Parks (MT FWP) received public comments that attached algae were growing in excess in the Smith River. DEQ developed a project team to investigate potential candidate causes for the undesirable algae levels and conducted datacollection work from 2018 through 2020. The results of this study are summarized in a parallel document (2018-2020 Smith River Algae Study- DEQ, 2024).

The watershed has also gained public attention due to the Black Butte Copper Project (BBC Project), an underground copper mine proposed by Tintina Montana Inc. (Tintina) that would be located 15 miles north of White Sulphur Springs near Sheep Creek, a tributary of the Smith River. The BBC Project area is in the southern central portion of the Sheep Creek drainage, approximately 19 river miles upstream from the Smith River confluence. Direct impacts to the Smith River are not anticipated from the BBC Project, but DEQ recognized a lack of recent water quality data for the river when evaluating baseline conditions for the area. With the initiation of the algae study in the Smith River, DEQ recognized the opportunity to simultaneously collect information about major ion and metal concentrations over a fifteen-month period.

At the time of publishing this study (December 2024), no underground mining, water management or treatment, or water discharge activities have occurred at the BBC Project site. Preliminary site preparation, limited construction of surface features and access roads, and exploration drilling have occurred at the site. The legal challenges to DEQ's 2020 EIS and permit decisions were overturned by the Montana Supreme Court in February 2024. All permitted mining and water discharge activities for the BBC Project require monitoring in Sheep Creek and some of its tributaries to confirm Tintina's compliance with state requirements, far upstream from the confluence with the Smith River.

This report presents the findings of the 2018-2019 metals study and includes an updated Metals Assessment to determine attainment of numeric metals water quality standards as defined in Circular DEQ-7 (DEQ, 2019a). The data collection locations are shown in **Summary Figure 1**. Results from this study and data from the past decade show that metals concentrations are generally low throughout the Smith River, with the exception of aluminum and iron periodically not meeting the water quality standards for aquatic life at some locations.

- Seasonal dissolved aluminum increases are observed in the Smith River immediately downstream of Sheep Creek, a tributary known to contain elevated aluminum concentrations from natural sources, but concentrations become diluted and comply with the standard at downstream locations. The frequency of Smith River samples not meeting the water quality standard for dissolved aluminum does not warrant an impairment listing (<10% of samples >87 µg/L).
- Total iron concentrations increase in the lower reaches of the Smith River throughout the year, from the confluence of Hound Creek to the mouth of the Smith at the Missouri River confluence, with the highest concentrations typically occurring during spring runoff. The frequency of Smith River samples not meeting the water quality standard for total iron warrants an impairment listing (13.5% of samples $>1,000 \mu g/L$).

Some tributaries to the Smith River contribute to changes in metals and chemical characteristics at low concentrations, likely reflecting the natural weathering of different geologic formations along with historical and ongoing human disturbance activities within the watershed. General trends are shown in **Summary Figure 1**, indicated with arrows and text boxes.

- The geothermal system near White Sulphur Springs contributes elevated concentrations of barium, bicarbonate, chloride, potassium, selenium, sodium, strontium, sulfate, and hardness to the South Fork of the Smith River, but these constituents become diluted further downstream.
- Geologic conditions in the Sheep Creek drainage contribute elevated aluminum and barium concentrations to the Smith River. Although other metals are low in Sheep Creek water samples, some benthic sediment metals (arsenic, chromium, copper, iron, mercury, and zinc) are elevated compared to Smith River sediment, but within levels established as natural background.
- The lower (northern) reaches of the Smith River are likely affected by changes in surrounding geology and erosion, as well as increased human disturbance activities that can contribute to sediment and low-level metals transport, like agriculture, residential development, and mining (historic and modern).
- In addition to periodically not meeting the water quality standard for total iron, water samples in the lower Smith River showed low-level increases for total suspended solids, hardness, sulfate, barium, copper, lead, manganese, and zinc, while the benthic sediments showed increased arsenic, cadmium, copper, iron, and zinc compared to other Smith River sediment samples.

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ACRONYMS AND ABBREVIATIONS

1.0 INTRODUCTION

This section provides background about the reasons the study was initiated, the selection of parameters and sampling locations, and study objectives.

1.1 STUDY BACKGROUND

The Smith River is an important recreational, agricultural, and ecological resource in Montana, with its stunning scenery and renowned trout fishery. Due to its popularity and importance to recreators, it is currently the only river in Montana requiring a floater's permit. In the past decade, Montana Fish, Wildlife and Parks (MT FWP) has typically received 10,000 or more float applications annually, and usually awards around 1,000 permits for the main float season (April through July). In 2015, the Montana Department of Environmental Quality (DEQ) and MT FWP began receiving public comments that attached algae were growing in excess in the Smith River. These comments continued through the 2016 and 2017 floating seasons. DEQ developed a project team to investigate potential candidate causes for the undesirable algae levels and conducted data-collection work from 2018 through 2020. The results of the algae study are summarized in a parallel document called the 2018-2020 Smith River Algae Study (DEQ, 2024).

The watershed has also gained public attention due to the Black Butte Copper Project (BBC Project), an underground copper mine proposed by Tintina Montana Inc. (Tintina) that would be located 15 miles north of White Sulphur Springs near Sheep Creek, a tributary of the Smith River. The BBC Project area is in the southern central portion of the Sheep Creek drainage, approximately 19 river miles upstream from the Smith River confluence.

An Environmental Impact Statement (EIS) was finalized by DEQ in 2020, followed by the issuance of a Hard Rock Mining Operating Permit under the Metal Mine Reclamation Act (MMRA), a Montana Air Quality Permit, a Montana Pollutant Discharge Elimination System (MPDES) permit, and a Construction Storm Water Permit under the Montana Water Quality Act. The EIS includes a multidisciplinary analysis of potential impacts to a broad range of environmental resources and receptors, including the surface waters located closest to the BBC Project, which consist of Sheep Creek and its tributaries: Coon Creek, Brush Creek, Little Sheep Creek, and Black Butte (also known as Big Butte) Creek. The EIS and related permits consider operational practices that are necessary for Tintina to comply with water quality standards and non-degradation criteria, which includes any necessary flow augmentation in affected streams in conjunction with separate authorization from the Department of Natural Resources Conservation (DNRC) to address the BBC Project's water use.

Direct impacts to the Smith River are not anticipated from the BBC Project, but DEQ recognized a lack of recent water quality data for the river when evaluating baseline conditionsfor the area. With the initiation of the algae study in the Smith River, DEQ recognized the opportunity to simultaneously collect information about major ion and metal concentrations over a fifteen-month period. Sampling events for major ions and metals were conducted in conjunction with the algae study during 2018 and 2019 in accordance with annual sampling and analysis plans (SAPs), although this timeframe was shorter than the algae study that extended into 2020.

No underground mining, water management or treatment, or water discharge activities have occurred at the BBC Project site at the time of publishing this study (December 2024). Preliminary site preparation, limited construction of surface features and access roads, and exploration drilling have occurred at the site. Mineral exploration in the Sheep Creek area occurred in the late 19th century, while modern exploration activities in the BBC Project area began in the mid-1970s and continued through the late

1980s. Additional exploration conducted by Tintina or earlier versions of the company began in 2010, resulting in an application for a Hard Rock Mining Operating Permit in 2015. Applications for air- and water-related permits were submitted to DEQ over the next three years and DEQ completed the Final EIS for the BBC Project in March 2020. Initial site preparation and construction activities took place between August and December 2020, while the legal challenges filed during that time with the Fourteenth Judicial District Court in Meagher County (District Court) resulted in a ruling in July 2022 that invalidated the mining permit. An appeal was filed with the Montana Supreme Court and a decision was issued in February 2024, reversing all counts of the District Court ruling, and the permit was reinstated in April 2024. All permitted mining and water discharge activities for the BBC Project require monitoring in Sheep Creek and some of its tributaries to confirm Tintina's compliance with state requirements, far upstream from the confluence with the Smith River.

This report is not a comprehensive review of all historic data for the Smith River or its tributaries, nor should it be interpreted as a baseline description of a pristine or purely natural setting. In addition to ongoing geologic weathering and erosion processes, water quality can be influenced by sediment or metals sourced from a wide range of human activities like agriculture, mining, residential development, recreation, or other activities that disturb streambanks, streambeds, or other surfaces on the landscape that are susceptible to erosion. These activities have occurred in the Smith River watershed primarily since the expansion of white settlement on Blackfeet territory and other tribal lands in the mid- to late-19th century (FWP and OPI, 2010), and similar development and land use is likely to continue in the future.

This report presents the findings of the 2018-2019 metals study and includes an updated Metals Assessment to determine attainment of numeric metals water quality standards as defined in Circular DEQ-7 (DEQ, 2019a). This report provides initial interpretations of potential seasonal and spatial trends based on a limited data set. Further study and sampling from additional tributaries and other locations in the watershed would refine the understanding of metals loading to the Smith River.

1.2 GENERAL STUDY OBJECTIVES

As described in the SAP documents developed for assessing metals (DEQ, 2018; DEQ, 2019), DEQ formulated two overarching study objectives:

- 1. Collect baseline data to describe the current physical and chemical conditions, and the concentrations of major ions, dissolved organic carbon (DOC), and metals in the Smith River. Sampling would be concurrent with the Smith River Algae Study and would occur at multiple sites during high- and low-flow months.
- 2. Provide baseline water quality data for the Smith River for potential future analysis of the existing environment and effects from tributaries on the mainstem, particularly Sheep Creek. Provide background information that may benefit other environmental analyses in the watershed.

1.3 PARAMETER SELECTION

A review of the Storage and Retrieval (STORET) and National Water Information System (NWIS) databases provided a summary of the data available for the Smith River for the decade prior to initiating this study in 2018. All data were obtained through studies conducted by DEQ and United States Geological Survey (USGS) (Caldwell and Eddy-Miller, 2013). Monitoring was previously limited to 18 sites on the mainstem of the Smith River, eight of those sites were monitored only for flow, pH, and total suspended solids (TSS), while a limited list of ions and metals was analyzed for samples collected from the remaining ten sites. A summary of the water quality data available for Smith River sites for the period between 2008 and 2017 is shown in **Table 1-1**.

Parameter	Number of Samples	Number of Unique Locations			
pH	15	9			
Aluminum (D)	3				
Arsenic (TR)	33	10			
Barium (TR)	3				
Manganese (TR)					
Strontium (TR)	3				
Potassium (TR)	3				
Sodium (TR)					
Hardness (Calcium + Magnesium) and Metals (Cadmium, Chromium, Copper,					
Iron, Lead, Selenium, Silver, Zinc) (TR)					

Table 1-1. Water quality data from the mainstem of the Smith River between 2008 and 2017.

TR = total recoverable, D = dissolved.

Other common parameters like alkalinity, chloride, and sulfate were not measured.

In comparison, more water quality data have been collected from Sheep Creek and its tributaries through baseline monitoring conducted by Tintina for the BBC Project (2011 to present) and DEQ for investigations related to two Total Maximum Daily Load (TMDL) reports (Section 2.2.3). The results for the Sheep Creek drainage indicated that the primary stream, and tributaries like Moose Creek and Black Butte Creek, have elevated concentrations of dissolved aluminum (exceedance rate >10%). The TMDL report that was developed by DEQ in 2020 concluded that aluminum in the Sheep Creek drainage is likely from weathering of natural sources and unrelated to land disturbances from historic or abandoned mines, or the limited active mining in the watershed (DEQ, 2020). Other metals (antimony, arsenic, cadmium, chromium, copper, lead, mercury, selenium, silver, thallium, and zinc) were typically below minimum calibration (reporting) limits for most of the sampling locations within Sheep Creek and its tributaries. Except for aluminum and arsenic, the concentrations of those metals were also below reporting limits for the historic Smith River samples.

Physical and chemical parameters like temperature, pH, alkalinity, hardness, dissolved oxygen (DO), and DOC are known to affect the solubility and mobility of ions and metals, so they were also measured *in situ* or analyzed from the same water samples collected for metals analysis. These data provide insight about the potential mechanisms for changes in ion and metal concentrations at different locations and flow conditions. Samples for major cations (calcium, magnesium, sodium, potassium) and anions (bicarbonate, sulfate, chloride) were included with the trace metals to provide background data for the relatively soluble constituents that originate from various geologic settings in the watershed. Samples were collected according to the methods established in the "Water Quality Planning Bureau Field Procedures Manual for Water Quality Assessment Monitoring" (DEQ, 2012).

Parameter lists for benthic (streambed) sediment and water samples analyzed in this study are provided in **Table 1-2** and **Table 1-3**. To observe potential changes at very low concentrations, analytical data for this study were reported by the laboratory to the lowest method detection limit when possible, rather than the higher reporting limit (i.e. "J flag" data). When applicable, water quality data are evaluated against the numeric standards for human health and aquatic life that are provided in DEQ Circular 7 (DEQ-7, 2019a). Samples were also collected from benthic or streambed sediments, in order to assess the metals concentrations and potential sources of adsorbed species or particles that may be entrained in the water column. Sediment metals data are evaluated against screening criteria endorsed by the National Oceanic

and Atmospheric Administration (NOAA, 2008; Table 4.4-1).

As described in the Introduction, DEQ's Water Quality Planning Bureau (WQPB) conducted a simultaneous study to investigate potential candidate causes for the undesirable algae levels, including nutrients (nitrogen and phosphorous), pH, hardness, discharge hydrologic analysis, water temperature, and tributary effects. The sampling period for this study extended beyond the timeframe for the metals sampling events, so additional information can be found within the Smith River Algae Study (DEQ, 2024). Data quality control is performed by the WQPB's data management and quality control (QC) systems prior to release to project staff for data use. A summary of statistical information for this study is provided in Section 4.

Parameter	Preferred	Alternate	Req. Report Limit			
	Method	Method	μ g/L			
Sediment Sample - Total Recoverable Metals						
Total Recoverable Metals Digestion	EPA 200.2		N/A			
Arsenic	EPA 200.8	EPA 200.9	1			
Cadmium	EPA 200.8	EPA 200.9	0.2			
Chromium	EPA 200.8	EPA 200.7	9			
Copper	EPA 200.8	EPA 200.7	15			
Iron	EPA 200.7	EPA 200.7	10			
Lead	EPA 200.8	EPA 200.9	5			
Zinc	EPA 200.7	EPA 200.7	20			
Sediment Sample - Total Metals						
Mercury	EPA 7471B		0.05			

Table 1-2. Benthic Sediment Parameter List, Analytical Methods, and Reporting Limits

Table 1-3. Water Quality Parameter List, Analytical Methods, and Reporting Limits*

*Total Recoverable samples preserved with nitric acid. Dissolved samples filtered in field (0.45 µm) and preserved with nitric acid. DOC samples filtered in field (0.45 µm) and preserved with phosphoric acid.

1.4 SITE SELECTION AND TIMEFRAMES

For ease of access and project logistics, the sites selected for metals sampling coincided with a subset of the sites being sampled for the Smith River Algae Study. **Table 1-4** provides a summary of the sampling sites, and **Figure 1-1** shows the locations within the Smith River watershed. These locations are distributed across different geologic formations, which can be separated into three primary regions, and provide insight into contributions from some of the primary tributaries (**Figure 1-2**).

From the confluence of the North and South Forks of the Smith River near the community of White Sulphur Springs, to the confluence with the Missouri River at the north end of the watershed, the Smith River extends approximately 125 river miles (**Table 1-4**), within a direct distance of approximately 100 miles. Data presented in the Smith River Algae Study were mostly collected along the float reach of the river, which extends for 59 river miles starting upstream at Camp Baker and ending at Eden Bridge. These locations are shown as sites 11M and 26M, respectively, in both studies (**Figure 1-1 and Figure 1-2)**. Additional data were collected upstream and downstream of the float reach and in targeted tributaries.

Physical parameters were measured and samples were collected for major ions and metals during three sampling events in 2018 (August, September, October) and seven sampling events in 2019. The proposed sampling event in November 2018 was canceled due to inclement weather. Benthic sediment samples were collected during the August 2018 sampling event. The study was re-initiated in early May 2019, followed by sampling events in late May, June, July, August, September, and October. Due to the number of sites being sampled and the distance between sites, each sampling event occurred over multiple days. There were a few cases where site access, safety, or weather conditions prevented sampling from taking place, examples include:

- Smith at Camp Baker (11M)- no metals sample or flow measured in July 2019;
- Smith at Castle Bar Road (17M)- no flow measured for any events, no metals sample in October 2018, early May 2019, August 2019, and October 2019.
- Sheep Creek (12T)- no flow measurements from September 2018 through June 2019.
- Smith near Mouth (27M)- no flow measurements except for July 2019 and October 2019.

The information collected through this metals study supplements the data from the Smith River Algae Study. This metals study report includes field parameters from 2018 and 2019 to provide context for trends in metals, but the complete data set from this timeframe and related discussion are provided in the Smith River Algae Study (DEQ, 2024).

Figure 1-1. Monitoring sites in the Smith River watershed presented in this report, including flow gages, water quality samples, and sediment samples. Field parameters were collected at additional sites in the mainstem and in tributaries, as part of the Smith River Algae Study. See Table 1-4 for site descriptions, primary tributary creeks are also labeled.

Figure 1-2. Metals monitoring sites in the Smith River watershed, shown over generalized regional geology. Abandoned mine sites are defined only as coal or non-coal, but post-1971 (modern) mining sites include Small Miner Exclusions (< 5 acres in size), Exploration Licenses, Hard Rock Mining Operating Permits (gypsum, copper, iron, and rock products), and Opencut Permits (sand and/or gravel). The post-1971 locations have had some degree of activity in the past 50 years, but the majority are not currently active.

Table 1-4. Sampling Sites and Descriptions*

eam of Cooks Creek and North Fork confluence. A Springs and eventually discharges to the South Fork.

I of the watershed and the two source water forks, prior to n basement rock and Paleozoic sedimentary units that may diments and fill.

above the confluence with Sheep Creek, while also rainages known to have historic mining activity. This site

from this tributary prior to the confluence with the Smith m in this watershed, as a result of natural processes and the

bove the Smith River confluence. With similar geologic been used in previous investigations as a background reek TMDL- DEQ, 2020).

Fenderfoot Creek, which has less historic human rtion of the watershed. This tributary is monitored for Project.

* Map Site Labels are not necessarily numbered sequentially, but metals sample locations correspond to the locations identified in the Smith River Algae Study.

** Sample Types are FP = Field Parameters, W = Water sample for ions and metals, S = Sediment sample for metals.

confluence with Hound Creek. This area consists of Jurassic disturbed by coal mining. Continuous discharge data are

study. It represents conditions above the confluence with Iing Coulee, which is another area historically disturbed by

2.0 BACKGROUND INFORMATION

This section includes details about existing hydrologic and geologic conditions in the Smith River watershed, which provide context for the interpretation of results from this study.

2.1 HYDROLOGIC BACKGROUND

2.1.1 Stream Classification and Impairment

Stream classification is the designation of a single or group of uses to a waterbody based on the potential of the waterbody to support those uses. Designated uses, or beneficial uses, are simple narrative descriptions of water quality expectations or water quality goals. Montana waters are classified for multiple uses. The Smith River and Sheep Creek are both classified as B-1, which specifies that the water must be maintained suitable for the following uses (Administrative Rules of Montana- ARM 17.30.623):

- Drinking, culinary, and food processing purposes, after conventional treatment (Drinking Water)
- Bathing, swimming, and recreation (Primary Contact Recreation)
- Growth and propagation of salmonid fishes and associated aquatic life, waterfowl, and furbearers (Aquatic Life)
- Agricultural and industrial water supply

While a waterbody might not actually be used for a designated use (e.g., as a drinking water supply), its water quality still must be maintained suitable for that designated use. DEQ's water quality assessment methods are designed to evaluate the most sensitive uses for each pollutant, thus ensuring protection of all designated uses (DEQ, 2021). Portions of the Smith River are listed as impaired because they do not meet all numeric water quality standards, as summarized in the following table (DEQ, 2021).

Stream Reach	Length (miles)	Impairment Cause(s)	Non-Pollutant Cause(s)	Source(s)
North and South Forks to Hound Creek	98.1	Total phosphorous and Escherichia coli (E. Coli)	Flow Regime Modification	Crop Production (Irrigated), Rangeland Grazing, Agriculture
Hound Creek to mouth at Missouri River	24.1	Total phosphorous, Temperature	Flow Regime Modification, Other anthropogenic substrate alterations, Physical substrate habitat alterations, Alteration in streamside or littoral vegetative covers	Grazing in Riparian or Shoreline Zones, Crop Production (Irrigated), Rangeland Grazing, Agriculture

Table 2-1. Currently Listed Water Quality Impairments in Smith River

In addition to the impairments listed for Smith River, Sheep Creek is also listed as impaired due to aluminum and *E. Coli*. Further details are provided in the "Sheep Creek *E. Coli* TMDL and Water Quality Improvement Plan" (Total Maximum Daily Load; DEQ, 2017) and the "Sheep Creek Aluminum TMDL" (DEQ, 2020). The source of aluminum is attributed to natural background sources which mobilize aluminum under certain physical and chemical conditions (see Section 2.2.3).

2.1.2 Groundwater and Surface Water Interactions

During a drought that began in the late 1990s, streamflow in the Smith River was insufficient to meet irrigation demands, in addition to the needs for recreation and viable fish habitat. The U.S. Geological Survey (USGS) and the Meagher County Conservation District initiated a multi-year hydrologic investigation of the Smith River watershed in 2006. This investigation provided background information about the upper Smith River watershed, from the portions that include the North and South Forks, down to the stream gage directly below Eagle Creek (Site 06077200, **Figure 1-1**). This study also detailed groundwater and surface water interactions for the upper region, based on measurements of groundwater elevations, stream stage, and physical field parameters.

Groundwater flow within the Quaternary alluvium and Tertiary basin-fill sediments generally follows landsurface topography from the uplands to the alluvial valleys of the Smith River and its tributaries. Groundwater levels were typically highest in the in late spring or early summer within monitoring wells located adjacent to streams, resulting from recharge from snowmelt and local precipitation, leakage from losing streams and canals, and recharge from local flood irrigation. The effects of flood irrigation resulted in increased hydraulic gradients, and in some examples the gradient reversed direction at several monitoring sites coincident with the initiation of nearby flood irrigation. Groundwater levels declined in mid-summer due to groundwater withdrawals and reduced recharge from decreased precipitation, increased evapotranspiration, and reduced leakage from some streams during periods of low flow. Groundwater levels typically rebounded in late summer, a result of decreased evapotranspiration, decreased groundwater use for irrigation, increased flow in losing streams, and the onset of late-season flood irrigation at some sites. (All summarized from Caldwell and Eddy-Miller, 2013)

The effect of groundwater and surface water interactions is most apparent along the North and South Forks of the Smith River where the magnitude of streamflow losses and gains can be greater than the magnitude of flow within the stream. Net gains consistently occurred over the lower 15 miles of the South Fork, which include inputs from geothermal sources near White Sulphur Springs (described in Section 2.2). A monitoring site near the mouth of the South Fork gained during all seasons, while two upstream sites on the South Fork exhibited variable conditions that ranged from gaining during the spring, losing during most of the summer as groundwater levels declined, and then gaining conditions again in late summer. The North Fork is highly managed at times through reservoir releases and irrigation diversions may remove a large percentage of streamflow. The lowermost reach of the North Fork near its mouth can transition from a losing to gaining reach throughout the year. (All summarized from Caldwell and Eddy-Miller, 2013)

Groundwater and surface water interactions occur downstream from the confluence of the North and South Forks of the Smith, but are less discernible compared to the overall magnitude of the mainstem streamflow. During periods of limited diversion, the segment of the mainstem Smith River between the forks' confluence and Newlan Creek display variable gaining or losing trends, while this portion is a losing reach during irrigation season conditions. The segment of the mainstem between Newlan Creek and the stream gage below Eagle Creek and Sheep Creek is generally gaining during periods of limited diversion, while the same reach becomes losing during irrigation season. (All summarized from Caldwell and Eddy-Miller, 2013)

The USGS study results are limited and do not include locations downstream from Eagle Creek to the confluence with the Missouri River, so gaining or losing reaches were not identified or quantified for the rest of the river. With the absence of significant agricultural development in the middle third of the watershed, meteoric recharge and other natural hydrologic processes likely control the groundwater and surface water interactions. This portion of the watershed consists primarily of limestone, which may result in gaining or losing reaches due to relatively high transmissivity of the limestone and potential fracture- or karst-controlled flow. Based on observations and measurements from the Smith River Algae Study, the river in this portion of the watershed may receive a significant contribution of groundwater in the Deep Creek area. Some of the seasonal trends noted in the upper watershed due to irrigation diversions, groundwater usage, and recharge or return flows are also likely to occur in the agricultural lands in the northern third of the watershed. However, the different geologic units in this northern portion of the watershed contribute different constituents to water quality of the Smith River.

2.2 GEOLOGIC BACKGROUND

2.2.1 Smith River Area

Geology of the Smith River watershed can be divided into roughly three primary geologic regions, as shown in **Figure 1-2** (based on Nilges and Caldwell, 2012; modified from Ross, Andrews, and Witkind, 1955). As discussed in later sections, the water quality data for major ions and metals in the Smith River likely reflect a combination of natural weathering processes and human disturbance of the various geologic environments that are encountered throughout the watershed. Note that the legislation for modern mine permitting (hard rock, opencut, and coal) was enacted in 1971, which is the year used as a threshold to characterize historic versus modern sites for this study. The post-1971 mining locations shown in **Figure 1- 2** have had some degree of activity in the past 50 years, but the majority are not currently active.

The upper or southern third of the watershed is comprised of Precambrian and Cambrian meta-sedimentary bedrock (approximately 500 million to 1.4 billion years old), with occasional intrusive and volcanic igneous rocks (Cretaceous to Tertiary in age, <100 million years). Some of the primary bedrock units encountered in this portion of the watershed include the Newland, Pilgrim, Park, and Meagher Formations. Some areas of the bedrock may host metallic ore deposits, due to mineralization events that were either contemporaneous with deposition or formation (syngenetic) or associated with alteration from later igneous activity. Some of these deposits have been explored or developed by historic and modern mine operations, although typically at a small scale (see **Figure 1-2**). This geology also extends across some portions of the Sheep Creek watershed, where an active iron mine and proposed copper mine (BBC Project) are located.

In the upper portion of the Smith watershed, tributaries sourced from bedrock headwater areas flow through valley fill and alluvium comprised of Tertiary and Quaternary sediments, which underly the main stem of the river. These materials support agricultural operations and residential areas on the surface, in addition to hosting shallow groundwater resources necessary for such development. The mine sites under Opencut Permits in this region produce sand and/or gravel resources from unconsolidated materials, with relatively shallow ground disturbance. Many of the historic mines and modern Small Miner Exclusion operations (<5 acres) in this portion of the Smith River watershed were focused on developing shallow placer (alluvial) gold deposits, although very few of them have any current or recent activity.

Geothermal activity in the White Sulphur Springs area is a surface expression of a deeper convective system. The generalized model of this system indicates that cold meteoric water descends along thrust faults and fractures zones where it is heated by an anomalously high thermal gradient at depth, likely greater than 1,600 feet below surface (Gierke, 1987). The heated water ascends along north-trending faults near White Sulphur Springs, where it mixes with groundwater at intermediate depths and in near-surface unconsolidated aquifers. Some thermal water discharges as springs in the unconsolidated material, with inputs to the South Fork of the Smith River, while much of the water appears to flow laterally along permeable fracture zones and sandstones within the Greyson Shale (Gierke, 1987). In some areas, thermal water may be prevented from reaching shallow aquifers by Tertiary clay, suggesting that intermediate thermal reservoirs may be present in Tertiary bedded gravel deposits at depth.

To the north of the confluence with Sheep Creek, the Smith River enters a canyon made of massive gray limestone of the Lodgepole and Mission Canyon Formations of the Mississippian-aged Madison Group. The limestone is extensive across this middle portion of the Smith River watershed, while difficult topography limits the extent of human development and disturbance that is observed in other areas along the river. Other less-extensive sedimentary formations are present in this region further from the river, along with Quaternary alluvial sediments adjacent to surface water pathways. Some limited mining activity occurs in this middle third of the watershed but not immediately adjacent to the Smith River, like sand and gravel production from Opencut Permits and a Hard Rock Mining Operating Permit to provide gypsum for cement production near Three Forks, Montana. Based on observations and measurements from the Smith River Algae Study, the river in this portion of the watershed may receive significant contributions from groundwater, particularly in the Deep Creek area. This may be reflective of the high transmissivity of the limestone and potential karst-related pathways for flow.

In the northern (lower) third of the watershed, the landscape changes to primarily Jurassic and Cretaceous sedimentary rocks above the confluence with the Missouri River. This geologic terrain is common across the plains of central and northern Montana. Quaternary sediments and alluvium occur in the floodplains adjacent to the Smith River and its tributaries. This northern region of the watershed supports increased agricultural, residential, and mining development compared to the middle region. These disturbance activities may increase the mobility of sediment containing metals or influence processes that control metals transport in water. The Smith River Algae Study notes that the final reach of the Smith River near the mouth is often very turbid and may sometimes contain increased total phosphorous concentrations. Coal production also occurred in this region from the 1880s to the 1940s, while modern mining activities include Opencut Permits and Hard Rock Mining Operating Permits (rock products, dimensional stone), with relatively shallow surface disturbance. As noted in the previous section, other human activities that influence water quality include alteration of streamside and riparian areas, crop production, grazing, residential development, and other substrate disturbance.

2.2.2 Smith River Coal

Notable medium-grade bituminous coal beds occur at the top of the Morrison Formation (late Jurassic), directly beneath the interbedded sandstone and shale of the Kootenai Formation (early Cretaceous). This region forms the southern edge of the Great Falls Coal Field, which extends across east-central Cascade County through communities like Stockett, Sand Coulee, and Belt. The coal may be exposed at the surface or deeply buried, in the Belt area it occurs roughly between 230 and 310 feet from surface. The coal is relatively thin across the region, with an average thickness of 8.5 feet near Sand Coulee and 4.5 feet near Belt (Rossilon et al, 2009).

The coal-bearing zone is exposed in many places in areas bordering the Smith River and its tributaries. Several coal mines were developed in the Hound Creek and Ming Coulee areas in the late 1800s. As reported by the USGS in 1906:

"The coal has been mined intermittently throughout this district for over twenty-five years, and within the last decade extensive prospecting has been done in order to ascertain the extent of the coal bed in this portion of the Sand Coulee basin. Several small mines are now operated, and there are a few abandoned mines from which coal is occasionally taken. Those worked are the Gibson, Carville, Patterson, Bickett, and Love mines. These have a combined annual output of only a few hundred tons" (Fisher, 1906).

The intermittent production from these mines increased by 1909, with reported annual totals of 1,800 tons at Carville Mine and 1,200 tons at Gibson Mine (Fisher, 1909). The USGS further noted:

"The valley of Hound Creek also exposes the workable coal of the lower part of the Kootenai for about 1 mile above its mouth, and the largest mine in the Smith River district is located on this tributary. From the east, three intermittent streams enter Smith River: Boston, Ming, and Goodwin Coulees. In the upper part of Ming Coulee, in the vicinity of Eden, the valley exposes the coal measures, and here a number of small mines have been opened. The same is true in the upper part of Boston Coulee."

"The large flow of water in Smith River is also an important consideration in the development of this coal district, for the percentage of impurities present in the coal is sufficient to render washing necessary before it can be successfully placed on the market. In neither Boston nor in Ming coulee is there sufficient water to wash the coals that could be mined from them, but the impurities might be removed by a dry washer process such as is now employed at Stockett."

These impurities include sulfur in the form of pyrite (iron sulfide, FeS₂), with an average content of 3% within the coal. Pyrite nodules up to 4 inches in diameter have been documented throughout the Great Falls Coal Field (Rossilon et al, 2009). Through mining and processing, the excavated coal beds and associated waste materials were exposed to oxygen and water, and the subsequent oxidation of pyrite resulted in acid rock drainage and water quality degradation that continues across portions of the Great Falls Coal Field (Duaime et al, 2004). In addition to releasing acidity, iron, and sulfate, the acid rock drainage may mobilize other ions or metals that occur as impurities within the pyrite or as minor constituents within the coal or adjacent lithology. Shallow or exposed coal deposits may also undergo some degree of pyrite oxidation and generate acidity in the absence of mining disturbance, if there is sufficient flow of oxygen and water through the material. The released metals may persist in the environment as mineral precipitates on rock surfaces or sediment, and/or complexed with organic material. Due to various disturbances or changes in physical or chemical parameters, these metals may be remobilized and influence water quality.

Detailed information is unavailable about the water quality or quantity of potential discharges from specific mines or *in situ* oxidation of coal deposits within the Hound Creek or Ming Coulee drainages, but as discussed later in this report, the low-level increases in metals concentrations observed in the lowermost reaches of Smith River may indicate influence from some of these sources.

2.2.3 Sheep Creek Area

The Sheep Creek drainage area consists primarily of shallow sediments on top of bedrock that ranges from Precambrian metasediments (Belt Group) that formed in a trough known as the Helena Embayment, to Cretaceous and Tertiary igneous rock intrusions and volcanic units. This area is similar to some of the upper portions of the Smith watershed and some of the mineralization contributes to the chemical signatures of Sheep Creek and its tributaries. For example, multiple zones of underground sulfide mineralization have been identified in the central portion of the Sheep Creek drainage area, including minerals like pyrite (FeS₂), chalcopyrite (CuFeS₂), tennantite (Cu₃(As,Sb)S₈), siegenite ((Ni,Co)₃S₄), cobaltite (CoAsS), and other amorphous phases bearing arsenic, copper, cobalt, and nickel. There are other locations nearby that contain an oxidized iron capping layer (gossan) at the surface (Tintina, 2017), which is also the source of iron ore at the Black Butte Iron Mine. Given the age of the sulfide mineralization that formed along a sea floor setting (approximately 1.4 billion years old), the occurrence of gossan in this region indicates the uplift, exposure, and natural weathering reactions of sulfide minerals. This oxidation would have produced acidity and mobilized metals and other elements over vast geologic time scales, contributing to the flux of mineral precipitates and sediments that influence the baseline characteristics of the watershed.

The Sheep Creek TMDL study considered potential sources contributing aluminum to Sheep Creek. Historical mining in the Sheep Creek watershed was limited (**Figure 1-2**) and the records for the known sites (Iron Cliff Mine, Virginia Mine) indicate an insignificant amount of underground and surface disturbance. Current active mining in the Sheep Creek watershed is also limited. The Black Butte Iron Mine has an active Hard Rock Mining Operating Permit and it provides iron oxide for cement production at facilities near Three Forks, Montana. The permit area encompasses approximately 118 acres, with 7 acres of actual surface disturbance. Approximately two miles to the east of the Black Butte Iron Mine, the Black Butte Copper (BBC) Project has conducted exploration drilling in small areas on the surface since 2010, while the associated Hard Rock Mining Operating Permit covers 1,888 acres, with 311 acres of actual disturbance. DEQ issued a Final EIS and associated permits for the BBC Project in August 2020, followed by legal challenges that were

overturned by the Montana Supreme Court in February 2024. The samples collected through this study represent the period before any construction or mining activity occurred. The BBC Project continues to be under preliminary construction as of 2024, so the full extent of permitted surface disturbance, underground mining, water management and treatment, and water discharge activities have not occurred.

Based on water quality data collected by DEQ, the Sheep Creek TMDL study concluded that historical and active mine areas are not considered sources of ongoing elevated aluminum loading (DEQ, 2020; see Section 3.3.6). The Sheep Creek TMDL study concluded that the mobilization of aluminum in Sheep Creek appears to be related to natural weathering of shallow soil and rock deposits due to the infiltration of spring runoff. Despite the steep and rugged topography, the majority of the Sheep Creek drainage has been mapped with soils rated as having low and moderate-low erodibility, based on the Universal Soil Loss Equation (USLE) Kfactor (DEQ, 2020). Agricultural activities and stream bank erosion may contribute to the sediment disturbance and loads for other metals within the Sheep Creek drainage. As described in later sections, some of the metals identified through geologic investigations can be traced in Sheep Creek water quality, but weathering and mobilization mechanisms do not affect all minerals or metals equally.

3.0 RESULTS AND DISCUSSION

3.1 GENERAL SUMMARY

Results for major ions, metals, and field parameters are presented in the following sections for the samples collected in August through October 2018 and May through October 2019. Field parameters were measured as part of the Smith River Algae Study at additional locations from May through October 2018 and May through October 2019 (see **Figure 1-1**). The multi-day sampling events are shown in the context of seasonal flow data for three USGS gage sites on the Smith River (**Figure 3-1**), which correspond to the locations shown on **Figure 1-1**.

The following data and figures reflect a series of physical and chemical factors that affect water quality during the year. These include increased flow and sediment transport during spring runoff, the dissolution of some constituents under various pH-controlled conditions (e.g. biological cycles, snow melt, mineral solubility, sulfide oxidation), irrigation diversions and eventual return recharge to the stream, dynamic groundwater and surface water connections, and potential influences from land disturbance related to agriculture and historical mining.

The Smith River is a calcium-magnesium-bicarbonate type water with moderately high alkalinity (100 to 272 mg CaCO₃/L) and sufficient buffering capacity to maintain pH levels between 7.68 and 8.87 (standard units.u.) in all mainstem reaches during the period of this study. The concentrations of major ions consistently decrease between the upper reaches and the final sampling point at the confluence with the Missouri River (bicarbonate, calcium, chloride, magnesium, sodium, sulfate). This trend reflects inputs from surface water tributaries and exchanges with groundwater systems over the approximate 125-mile length of the river. With a few exceptions, these inputs typically dilute the ionic signatures of the upstream Smith mainstem flow and the headwater sources, particularly the geothermal water influencing the South Fork of the Smith.

In addition to spatial changes and tributary dilution, concentrations of major ions like calcium, magnesium, sodium, sulfate, and bicarbonate undergo dilution during seasonal high-flow periods in the spring and then tend to increase when flows return to base conditions in late summer and fall. However, the high-flow periods also increase erosion and scouring, which increases the concentrations of total suspended solids (TSS) and total metals within the river for a short time period, particularly aluminum, iron, and manganese. The dissolved fraction of these metals may also occur at relatively elevated concentrations due to

weathering of sediments and rocks by slightly acidic snow melt runoff in the spring. Most other metals occur at low concentrations in the Smith River, typically near or below the respective analytical method reporting limits (arsenic, cadmium, chromium, copper, lead, selenium, silver, and zinc). Other metals like aluminum, barium, iron, manganese, and strontium occur at slightly higher concentrations during periods of low flow, but often below numeric water quality standards. Spatial trends observed for some of these metals provide insight about potential loading from tributaries to the Smith, anthropogenic sources, and/or weathering from different geologic regions.

During a high-flow period in early May 2019, the chronic aquatic life standard for dissolved aluminum (87 µg/L) was exceeded in one sample from Sheep Creek (163 µg/L) and one sample from the Smith River directly below the Sheep Creek confluence $(142 \mu g/L)$. During three separate sampling events, the concentrations of total iron (a non-priority pollutant) in the Smith River exceeded the chronic aquatic life standard of 1,000 µg/L at the lower-most sampling point, directly upstream from the Missouri River confluence. Potential sources for these metals are described further in the sections below.

The concentrations of most metals in benthic (streambed) sediment in the Smith River were typically within the background ranges provided by NOAA, except for arsenic and zinc, which regularly exceeded the background ranges (NOAA, 2008). For other metals like cadmium, chromium, copper, and iron, the concentrations generally increased from upstream to downstream and the highest concentrations were observed at the lower sites. The sediment samples from Sheep Creek and Calf Creek (reference stream) had greater concentrations of arsenic, chromium, copper, iron, and zinc than any of the respective Smith samples. These trends likely reflect the weathering of geologic formations and mineralized areas within these drainages. The Sheep Creek TMDL report considered Calf Creek to be a "reference" site because it is in an area of the Sheep Creek watershed that is mostly undisturbed by human activities (DEQ, 2020).

3.2 TOTAL DISCHARGE (FLOW) RESULTS AND DISCUSSION

When possible, total channel discharge (flow) was measured at sampling locations that overlapped with the Smith River Algae Study. Methods included the quantitative flow meter method, the semi-quantitative float method (DEQ, 2012), or DEQ's acoustic Doppler current profiler (ADCP) for the mainstem Smith River. **Figure 3-1** depicts the daily mean flow during 2018 and 2019 for three USGS stream gage locations on the Smith River; 06076690 (Fort Logan, above Sheep Creek confluence), 06077200 (Devil's Bridge, below Sheep Creek and Eagle Creek confluence), and 06077500 (near Eden, above Hound Creek confluence).

Figure 3-1. Daily mean flow during 2018 and 2019 for three USGS stream gage locations on the Smith River. The first day for each metals sampling event is shown on the x-axis to indicate the flow conditions during each sampling event. The gage location name "bl Eagle Creek" means below the confluence.

The stream hydrograph for the Smith River is typical of many streams in Montana, with the highest flow conditions responding to runoff in late spring and early summer months, often exceeding 2,000 cubic feet per second (cfs). The Smith River Algae Study noted that during the first year of sample collection (2018), the river exhibited the third highest peak flow and longest runoff period on record since 1997. Baseflow conditions are observed later in the summer and fall months, although some slight increases in this time period may represent recharge return from irrigated agricultural lands. These trends are generally consistent with the conditions observed in the earlier study by USGS (Caldwell and Eddy-Miller, 2013). With the Fort Logan gage being the furthest upstream, the increase in flow between that site and the gage below Eagle Creek represents the flow contributions from Sheep Creek and Eagle Creek (difference between blue and red lines). Without isolated measurements from Sheep Creek or Eagle Creek, it is not possible to differentiate the separate contributions from these tributaries between the USGS gage sites.

3.2.1 Load Estimates

The extent of load analysis for each constituent and each stream reach or tributary is limited, due to the number of flow measurements that correspond with available water quality samples (see **Table 3- 1**). USGS flow data were used to calculate loads unless the only flow measurement was provided by DEQ. For overlapping measurements, the difference between the USGS gage and the DEQ manual measurements had an average difference of 9.6 cfs and average error of 2.5%. The load calculations are presented in **Appendix A** and the discussion about load trends has been consolidated into the discussion about concentration trends within the following sections.

Table 3-1. Flow data for 2018-2019; Comparison between USGS and DEQ measurements. Not all events had overlapping data to allow calculation of difference or error.

3.3 WATER QUALITY RESULTS AND DISCUSSION

3.3.1 Beneficial Use Assessment

DEQ's water quality programs aim to protect and improve water quality of state waters. An important step in achieving these goals is to assess current water quality conditions. The primary objective of water quality assessment is to determine whether waters are supporting each of their designated beneficial uses. Each use may be affected by multiple types of pollution, therefore, evaluating use support entails evaluating whether multiple water quality parameters associated with each use are meeting applicable water quality standards (Makarowski, 2020). Every two years, DEQ submits a revised list of impaired and threatened waters to Environmental Protection Agency (EPA) via Montana's Water Quality Integrated Report as directed by the Montana Water Quality Act (§ 75-5-702, Montana Code Annotated- MCA) and Section 303(d) of the federal Clean Water Act (33 U. S. Code § 1251).

A waterbody is considered impaired for a parameter if it does not meet water quality standards for that parameter. When any single parameter associated with a beneficial use is impaired, the use is not fully supported. While DEQ's parameter-specific assessment methods guide impairment decisions for specific waterbody-parameter combinations, they individually do not allow an assessor to affirm that a use is fully supported. To affirm a use is fully supported, assessments for all core parameters associated with the use must be assessed and indicate non-impairment. In the case of aquatic life, direct measures of the use may be used to determine if the use is fully supported (Makarowski, 2020). Each surface water in Montana is classified according to the present and future beneficial uses it is expected to support (75-5-301, MCA).

The overall process used by DEQ to assess state waters and make consistent use support decisions is laid out in the Beneficial Use Assessment Method (Makarowski, 2020). This document describes aspects of assessment that are applied universally among parameter-specific assessment methods to limit redundancy and inconsistency among assessment methods.

3.3.2 Metals Assessment

Metals pollutants can adversely affect the beneficial uses for aquatic life/fish and human health. DEQ's Metals Assessment Method (Drygas, 2012) provides a method and monitoring framework to determine attainment of numeric metals water quality standards as defined in Circular DEQ-7 (DEQ, 2019a).

When assessing metals data, both the aquatic life/fish and drinking water beneficial uses are evaluated. Numeric standards to protect aquatic life and human health are different and therefore the methods on how they are applied differ (DEQ, 2019a). In general, some standard exceedances are allowed to assess the aquatic life/fish beneficial use, with the exception of silver, which is interpreted as a "not to exceed" value. No exceedances are allowed for the drinking water beneficial use (human health standard). Some of the aquatic life standards are dependent on hardness and adjust with changes to the hardness (Drygas, 2012).

Numeric standards for aquatic life support and human health are outlined in the Circular DEQ-7 (DEQ, 2019a). When making attainment decisions, the minimum sample size is 8 independent samples within the same assessment frame and data from the last ten years is used.

Aquatic life standards are for both acute and chronic exposure and the Metals Assessment Method allows for a 10% exceedance rate. This means that if more than 10% of the samples exceed the standard, then the attainment decision is to list or to remain listed (Drygas, 2012). However, there are three exceptions to the 10% exceedance rate attainment decision: 1) silver must not exceed the acute standard; 2) the attainment decision is to list or to remain listed regardless of the percent exceedance by the data set or the data set size if twice the acute standard is exceeded in a sample; 3) if the 10% exceedance rate threshold is surpassed but no human caused metals sources are found in the drainage, then this shall be reviewed by management for a case by case basis. No standard exceedances are allowed when assessing for human health. Guidelines on beneficial use attainment are outlined in more detail in the Metals Assessment Method (Drygas, 2012).

The Smith River is split up into two assessment units, which are unique identifiers that segment the waterbody based on certain characteristics such as changes in ecoregion, changes in land use and/or land cover, sources of pollution, or shifts in slope. One assessment unit encompasses the Smith River from the North and South Forks to the confluence with Hound Creek (MT41J001_010). The other assessment unit encompasses the Smith River, from Hound Creek to the mouth, at the Missouri River (MT41J001_020). Impairment decisions are applied to these assessment units.

Preliminary assessment of metals data from 2013 to 2023 shows an exceedance rate of 1.96% for the chronic aquatic life/fishes standard for dissolved aluminum and 1.47% for the chronic aquatic life/fishes standard for iron for the North and South Forks of the Smith River to its confluence with Hound Creek (MT41J001_010). Metals data for this assessment unit was below the allowable 10% exceedance rate for both acute and chronic aquatic life standards.

Whereas, for that same ten-year timeframe, preliminary assessment of metals data for the assessment unit that encompasses the Smith River from Hound Creek to its mouth at the Missouri River (MT41J001_020), shows an exceedance rate of 13.51% for the chronic aquatic life/fishes standard for iron, which is greater than the allowed 10% exceedance rate. Montana will list this segment of the Smith River for Iron as a category 5 listing in the next Integrated Report. A category 5 listing means one or more applicable beneficial uses have been assessed as being impaired or threatened, and a TMDL is required to address the factors causing the impairment or threat.

Final impairment listings will be available with the next Integrated Report and are contingent on federal approval.

3.3.3 Spatial Trend Interpretation

The example shown in **Figure 3-2** provides context for the spatial trend graphs that are shown elsewhere in this report. Each rectangular portion of the graph represents a sampling event under the respective dates, moving downstream from left to right on the x-axis in each example. Each sampling location is shown based on the river-mile distance below the confluence of the North and South Forks of the Smith River. The colored segments correspond to the generalized geologic units shown in **Figure 1-2**. Although this color scheme is not shown on each figure, this geologic background should be considered when interpreting the following water quality results. These units may contribute to the sediments, ions, and metals observed in the Smith River and its tributaries.

Figure 3-2. Example of spatial trend graphs contained in this report, with background colors depicting the primary geologic regions in the watershed from left to right on the x-axis. Although this example shows Specific Conductivity data, the units and scale of the y-axis are not important for this explanation. The symbols for the 2018 and 2019 data from the Smith River and its tributaries are explained in the key.

3.3.4 Field Parameters

Field parameters were measured as part of the Smith River Algae Study at many locations from May through October 2018 and May through October 2019 (**see Figure 1-1**). These locations included the North and South Forks of the Smith River, some of the primary tributaries, and locations above and/or below tributaries when possible. Although samples were not collected to characterize major ions and metals at all sites, the field parameters provide supplemental insight about spatial trends in physical and chemical conditions that may influence metal mobility. The measurements for all mainstem locations on the Smith River are summarized in **Table 3-2**, along with Sheep Creek in **Table 3-3**, and all other tributaries in **Table 3-4**.

Table 3-2. Field Parameters- Smith River, all mainstem locations. Parameters measured from May through October 2018 and May through October 2019. Locations and dates extend beyond the complete samples for ions and metals.

Table 3-4. Field Parameters- Smith Tributaries, excluding Sheep Creek. Parameters measured from May through October 2018 and May through October 2019. Locations and dates extend beyond the complete samples for ions and metals.

Table 3-5. Field Parameters - White Sulphur Springs (Spa Motel), the geothermal source that contributes to the South Fork of the Smith River. The total concentration is shown for each analyte unless noted otherwise. Samples collected on 3/29/2011 as part of geothermal survey conducted by Montana Bureau of Mines and Geology (MBMG), from Ground Water Information Center (GWIC) database.

Alkalinity, pH, and Dissolved Oxygen (DO)

As shown in **Table 3-2**, **Table 3-3**, and **Table 3-4**, the Smith River and its primary tributaries consistently maintained a slightly alkaline pH during this period of study, with measurements ranging between 7.50 and 8.87 s.u. for all streams. Sufficient inorganic carbon is available in these streams, primarily as bicarbonate, to neutralize potential sources of acidity and to buffer any significant changes to pH. Some of the tributaries had lower alkalinity concentrations than the mainstem Smith River sites (<100 mg/L), while others like Benton Gulch (Thomas and Cottonwood Creeks) and the South Fork of the Smith River had some of the highest alkalinity concentrations measured (>280 mg/L).

Many investigations have documented that natural aquatic systems can exhibit significant diel (24-hour) or diurnal fluctuations in pH, dissolved oxygen (DO), inorganic carbon, and organic carbon that are largely driven by biological activity. Aquatic plants and micro-biota may consume or produce carbon dioxide and DO, depending on whether photosynthesis or respiration is the dominant process at the time (Odum 1956; Pogue and Anderson 1994; Nagorski et al. 2003; Parker et al. 2005, 2007a). These short-term fluctuations are driven by the daily photoperiod, which can influence instream temperature, nutrient and carbon cycles, dissolved gas gradients between air and water, and the pH and oxidative conditions that may control the solubility, adsorption, or mobility of metals and metalloids (e.g., Nimick et al. 2003, 2005; Gammons et al. 2005; Parker et al. 2007a, b and references therein).

For the high-flow months, the measured pH values ranged no more than 0.5 s.u. within all primary tributaries and between the upstream and downstream locations on the Smith River. For baseflow conditions during the warmer and more biologically active months, measured pH value ranged by no more than 1.0 s.u. between all sampling sites. With the dynamic nature of pH at any given site through the day, the measured values in this study may not represent the maximum or minimum values that occur, nor represent the range that might occur on a seasonal cycle.

Moderate to high DO concentrations were measured at all sites in the Smith River and its primary tributaries, typically between 8 and 12 mg/L for each monthly sampling event. Some of the higher DO measurements occurred in months with lower water temperatures (increased DO solubility) and reduced biological activity. With 226 measurements of DO concentrations taken during this study period, only three were below 7.3 mg/L (6.1, 6.5, and 6.9 mg/L), indicating that DO occurred near or above saturation throughout the sampling locations. With the dynamic nature of DO at any given site through the day, the measured values in this study may not represent the maximum or minimum values that occur, nor represent the range that might occur on a seasonal cycle.

Oxidation-reduction potential (ORP- or converted to "Eh") is a measurement of electron activity that relates to the relative amounts of available oxidant or reductant species within a water sample. Although ORP is not a direct measurement of DO concentrations, the ORP can be heavily influenced by DO and other oxidants. ORP was not directly measured in these studies, but the observed DO concentrations suggest a generally consistent oxidizing environment in these streams. With regard to metals and metalloids, the pH and oxidative conditions measured during this study are not conducive to significant metal solubility. Although acidic conditions can increase metal solubility and diminish the effects of surface adsorption, many metals form insoluble oxyhydroxides or carbonates within the observed alkaline pH and oxidizing conditions observed during this study period. It is also common for potentially mobile elements to adsorb or adhere to certain particles or sediments under these conditions, particularly the surfaces of manganese or iron oxyhydroxides and organic carbon (Eby, 2004). The observed variations in most metals concentrations do not appear to directly correlate with the minor fluctuations observed in pH or DO concentrations for the streams. However, there may be biologically driven fluctuations at the microscopic or molecular level that can mobilize adsorbed species.

Within the observed pH range, alkalinity is dominated by the concentration of bicarbonate (HCO3) in samples from all locations, which is more abundant than carbonate (CO_3^{-2}) in ratios from 8.5:1 to 150:1. Sources of inorganic carbon include gas exchange and weathering of minerals, particularly carbonates, which can be found in multiple geologic units that occur within the watershed (**Figure 1-2**). This alkalinity sufficiently buffers drastic changes in pH which might mobilize metals and chemical equilibria with bicarbonate precipitates often controls the concentration of dissolved ions or metals. Some of the spatial and temporal variations in alkalinity are noteworthy because they align with patterns observed for other major ions.

As shown in **Figure 3-3**, the total alkalinity concentration generally decreased with distance along the length of the Smith River during all monthly sampling events. This trend reflects inputs from surface water tributaries and exchanges with groundwater systems over the approximate 125-mile length of the river. Some of the highest alkalinity concentrations occurred in the upper reaches of the Smith River and in the upper tributaries like Benton Gulch (Thomas and Cottonwood Creeks) and the South Fork of the Smith River (>280 mg/L). Tributaries like Sheep Creek, Tenderfoot Creek, and Deep Creek had the lowest alkalinity concentrations that were measured, and dilution effects in the Smith River were observed in all sampling months. This seems counterintuitive given the abundance of carbonate rocks in this region, but the alkalinity load may be controlled by chemical equilibria or solubility limits. These tributaries join the Smith River approximately halfway along the watershed and the alkalinity in the remainder of the downstream Smith River samples remained below the concentrations measured in the upper reaches. Limited data from Hound Creek, which connects near the lower-most end of the Smith River, indicate elevated alkalinity in this tributary but with little to no effect on alkalinity in the Smith River.

Specific Conductivity (SC)

Similar to the trends in alkalinity, the SC generally decreased with distance along the length of the Smith River from upstream to downstream, reflecting inputs from surface water tributaries and exchanges with groundwater (**Figure 3-4**). As a proxy measurement for changing ion concentrations, the SC measurements also reflected dilution during seasonal high-flow periods and then increased when flows returned to base conditions.

Although some of the field parameter locations were not sampled for major iron or metals, the SC measurements provide a relative indicator of the constituents that occur at each location and the contributions from nearby tributaries. With few outliers, the highest SC measurements occurred in upper reaches of the Smith and in upper tributaries like Benton Gulch and the South Fork of the Smith River (typically >600 µS/cm). This part of the watershed includes variable geologic conditions, historic and smallscale mining, residential and agricultural development, dynamic groundwater exchange, and a geothermal signature influencing the South Fork of the Smith River (White Sulphur Springs, **Table 3-5**).
Tributaries like Sheep Creek, Tenderfoot Creek, and Deep Creek generally had the lowest SC measurements (100 to 300 µS/cm), and the dilution effects in the Smith River were observed in most sampling months. These tributaries join the Smith River approximately halfway along the watershed and the SC in the remainder of the downstream Smith River samples remained relatively constant and below the levels from the upper reaches. Although data from Hound Creek are limited, the SC measurements in this tributary are slightly higher than those in the Smith River above the confluence. In some months, minor increases in SC were observed at the lower-most two or three monitoring points on the Smith River.

Total Suspended Solids (TSS)

As noted previously, high-flow periods result in scouring, erosion, and increased TSS concentrations in the Smith River and individual tributaries (**Figure 3-5**). Some of the larger tributaries in the upper reaches of the Smith River (Newlan Creek, Beaver Creek, Camas Creek, and Benton Gulch), have some of the higher TSS concentrations measured during high-flow and low-flow periods. The streams in this area occur within unconsolidated valley fill, so the increased TSS likely reflects mobilization of streambed sediment, streambank erosion, and/or runoff from adjacent lands.

Sheep Creek, Tenderfoot Creek, and Deep Creek typically had the lowest TSS concentrations, although the TSS contribution from Sheep Creek during spring months corresponds with a significant dissolved aluminum component. Some of the TSS load estimates indicate that the contribution from Eagle Creek may be greater than Sheep Creek, since the downstream monitoring point (Devil's Bridge) had loads greater than the sum of Sheep Creek and the Smith River upstream of the confluence. There may be other tributaries or sediment sources that influence the Smith River downstream from this portion of the watershed, but changes in TSS are typically less significant through the areas dominated by limestone bedrock. Some of the dilution effects observed from these tributaries are less apparent for TSS than other parameters.

During both high-flow and low-flow periods, the TSS in the Smith River increased in the lowest reaches before the Missouri confluence. This seems to correlate with increased TSS in Hound Creek in some cases, however there may be other tributaries and/or runoff from adjacent lands that also contribute solid loads. This portion of the watershed consists of sedimentary rock types which may be more prone to erosion (e.g. sandstone, siltstone, shale). This area is also part of the northwestern great plains ecoregion, which has naturally higher erosion rates than the rocky mountains. The Smith River Algae Study notes that the final reach of the Smith River near the mouth is often very turbid (elevated TSS) and may sometimes contain increased total phosphorous concentrations. As noted previously, human activities that influence water quality include alteration of streamside and riparian areas, crop production, grazing, residential development, and other substrate disturbance. Coal deposits and historic coal mining in this area may also contribute to exposure of some reactive minerals and the occurrence of metals within sediments that may be mobilized. This is discussed further in other sections.

Figure 3-3. Alkalinity concentrations for the Smith River and tributaries, 2018-2019 events.

Figure 3-4. Specific Conductivity (SC) measurements for the Smith River and tributaries, 2018-2019 events. The lowest SC measurement shown for the Smith in June 2019 (94.1 µS/cm) was recorded for the site upstream of the Hound Creek confluence.

Figure 3-5. Total Suspended Solids (TSS) concentrations for the Smith River and tributaries, 2018-2019 events.

3.3.5 Major Ions and Dissolved Organic Carbon

As noted in the summary above, the Smith River is a calcium-magnesium-bicarbonate type water with moderately high alkalinity and sufficient buffering capacity to maintain neutral to slightly alkaline pH levels in all mainstem reaches (**Figure 3-6**). The concentrations of major ions are summarized in **Table 3-6**, **Table 3-7**, **Table 3-8, and Table 3-9**. Ion concentrations consistently decrease between the upper reaches and the final sampling point at the confluence with the Missouri River, most notably for bicarbonate, calcium, chloride, magnesium, sodium, and sulfate. This trend reflects inputs from surface water tributaries and exchanges with groundwater systems over the approximate 125-mile length of the river. These inputs typically dilute the ionic signatures of the upstream mainstem flow and the headwater sources, particularly the geothermal water chemistry influencing the South Fork of the Smith River. Samples were collected in 2011 as part of a survey conducted by Montana Bureau of Mines and Geology (MBMG). As shown in **Table 3-9**, the geothermal system has significantly higher concentrations of bicarbonate, chloride, potassium, sodium, and sulfate than any samples collected from the Smith or other tributaries in this metals study.

Figure 3-6. Trilinear (Piper) Diagram. The concentrations of different cations and anions are shown as relative percent abundance in the lower triangles. These are combined into the upper diamond to summarize the "water type." The Smith River and Sheep Creek would be considered a calciummagnesium-bicarbonate type, while the geothermal headwaters in White Sulphur Springs are a sodiumbicarbonate-sulfate type (MBMG, 2011 data).

In addition to spatial changes, major ion concentrations undergo dilution during seasonal high-flow periods and then tend to increase when flows return to base conditions. This seasonal trend is best demonstrated in a trilinear (Piper) diagram to summarize major ion ratios (**Figure 3-6**) and in the individual figures for chloride, hardness, sodium, and sulfate. In the trilinear diagram, the data for Sheep Creek consistently plot separately from the main stem of the Smith River. This indicates that Sheep Creek has relatively less sulfate and chloride, and the ion ratios do not undergo as much seasonal variation. Although the data for all Smith River samples are closely spaced, during low-flow periods there is a general shift to higher concentrations for most major ions and the ratios between ions also change (toward the top/right in **Figure 3-6** diagrams). Although major ion data are not available for the North and South Forks of the Smith River, the geothermal signature that influences the South Fork is also plotted for background comparison as a headwater source.

Bicarbonate

As shown in Table 3-6, Table 3-7, and Table 3-8, bicarbonate (HCO₃) is the most abundant anion in the Smith River and its tributaries. Concentrations in the Smith River ranged from 111 to 300 mg/L, while concentrations at the mouth of Sheep Creek and other tributaries ranged from 65 to 150 mg/L and 55 to 298 mg/L, respectively. Bicarbonate is the dominant inorganic carbon species for all sites, with minor concentrations of carbonate measured in some samples (**Table 3-6**, **Table 3-7**, and **Table 3-8**). Inorganic carbon equilibrium models demonstrate that bicarbonate is the dominant species between pH values of approximately 6.5 and 10.5, (Dasaard et al, 2016) which align with the conditions measured in this study. Like many freshwater bodies, bicarbonate is primarily responsible for buffering potential changes in pH due to incoming sources of acidity and alkalinity in the Smith River watershed. Bicarbonate concentrations are slightly higher than the total alkalinity concentrations shown in **Table 3-6**, **Table 3-7**, and **Table 3-8**, but the spatial and seasonal trends are very similar to those observed for alkalinity (Figure 4-3) and a separate graph for bicarbonate is not provided.

Chloride

Chloride is less abundant than other major ions, with relatively low concentrations $\left\{ \langle 11 \text{ mg/L} \rangle \right\}$ in all reaches of the Smith River (**Figure 3-7**). Chloride behaves as a conservative ion in aquatic settings, meaning its movement is not inhibited by interactions between water and soils, sediments, and rocks (Eby, 2004). This may be used as an indicator of influences from tributary dilution, exchanges with groundwater systems, and/or other sources of constituents in the watershed. Chloride reflects the common trend of decreasing concentrations between the upper reaches and the final sampling point on the Smith River, along with seasonal dilution during high-flow periods and increasing concentrations during base flow months. The elevated chloride concentrations in upper reaches of the Smith River, particularly during baseflow, may be a remnant from dilution of the geothermal system in the headwaters (169 mg/L).

The chloride concentrations at the mouth of Sheep Creek were lower than the concentrations observed in the Smith River during each sampling event (0.6 to 1.4 mg/L). The low chloride concentration from this tributary provides notable dilution to the Smith River, as observed in the downstream sites closest to the Sheep Creek confluence. Concentrations in the Smith River continue to decrease or remain at a lower level through the middle portion of the watershed. Slight increases are observed in the lower-most samples of the watershed across multiple sampling events. This may reflect another constituent released under the changing geologic conditions and anthropogenic inputs in the lower portion of the watershed.

Sulfate

Sulfate (SO_4^{-2}) is the second-most abundant anion in the Smith River and in Sheep Creek, with concentrations ranging from 15.5 to 79.5 mg/L and 3 to 7 mg/L, respectively (**Figure 3-8**, **Table 3-6**, **Table 3- 7**, and **Table 3-8**). Similar to other ions, sulfate exhibits decreasing concentrations between the upper reaches and the final sampling point on the Smith River, along with seasonal dilution during high-flow periods and increasing concentrations during base flow months. The elevated sulfate concentrations in upper reaches of the Smith River, particularly during baseflow, are likely remnant from dilution of the geothermal system in the headwaters (282 mg/L).

The low concentrations contributed by Sheep Creek provide more relative dilution during high-flow periods, as sulfate in the Smith River remains at a higher level in later months. Although some constituents in Sheep Creek like aluminum, barium, and iron reflect mineral weathering within the watershed, the consistently low sulfate concentrations are not indicative of significant oxidation of sulfide minerals. Although sulfate data were not collected at many lower locations, some of the increases near the end of the watershed likely reflect anthropogenic sources and geologic changes in the Hound Creek area. Changes in pH are not apparent due to the abundant alkalinity in the Smith River, but slightly increasing sulfate may indicate inputs from areas of sulfide mineral oxidation related to exposed coal or other iron-bearing deposits and historic mining activity.

Hardness and Cations

As shown in **Table 3-6**, **Table 3-7**, and **Table 3-8**, the abundance of cations in the Smith River and Sheep Creek can be generally ranked in decreasing order: calcium > magnesium > sodium > potassium. The low concentration of potassium throughout the Smith River (2 to 5 mg/L) and Sheep Creek (1 to 2 mg/L) in all sampling events makes it difficult to discern meaningful trends. In contrast, the spatial and seasonal trends observed for sodium are nearly identical to the trends in chloride (**Figure 3-7 and Figure 3-9**), although occurring at slightly higher concentrations (2 to 29 mg/L). Sodium concentrations exhibited dilution during high-flow periods, tributary dilution (especially from Sheep Creek), and dilution of the geothermal source at the headwaters (478 mg/L).

The calcium and magnesium concentrations show a slightly different trend than the monovalent ions. While the upper reaches still exhibit some of the highest concentrations followed by gradual dilution, the dilution effects from Sheep Creek are less pronounced. Below the Sheep Creek confluence, soluble calcium and magnesium may be sourced from mineral dissolution and potential groundwater inputs that occur within this portion of the watershed. Similar to other ions, there is a slight increase in the lowermost watershed samples during some events. When evaluated individually, the spatial and seasonal trends in calcium and magnesium align very closely, but within different concentration ranges. These trends also correspond with those observed for total hardness (**Figure 3-10**). This is no surprise as total hardness is sometimes defined as the sum of calcium and magnesium concentrations, but it also includes all other multivalent cations in a given sample (e.g. strontium, barium, trace metals, etc.). Like some other parameters previously discussed, there were more locations on the Smith River and its tributaries that were measured for hardness than sampled for ions and metals.

As depicted in **Figure 3-10**, hardness provides greater detail about potential sources and general trends for a range of ions. Upper tributaries like the South Fork, Newlan Creek, and Benton Gulch had elevated concentrations relative to the mainstem of the Smith River. The low concentrations in mid-region tributaries like Tenderfoot Creek and Deep Creek are similar to those observed for Sheep Creek, with lesser influence on the Smith River in this reach. The contributions from Hound Creek and adjacent areas resulted in increasing concentration at the lower end of the watershed.

Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) occurs at relatively low concentrations in the Smith River, ranging between 2.2 and 6.6 mg/L (mean of 3.7 mg/L) throughout the study period. The DOC concentrations in Sheep Creek are very similar, ranging between 2.4 and 5.6 mg/L (mean of 3.6 mg/L). For both streams, DOC concentrations are generally higher during high-flow periods and then decrease in later months (**Figure 3- 11**). This may reflect contributions from runoff and mobilization of organics during disturbance to streambed and channel margins. Higher DOC concentrations tend to occur in the upper reaches of the Smith River, with gradual reduction along the length of the watershed. Slight increases are observed in the lowermost site of the watershed during some months. This spatial trend may reflect the geologic conditions and level of agricultural disturbance across the watershed, with the upper third and lower third consisting of more easily eroded unconsolidated sediments and sedimentary rocks, and the middle portion consisting of exposed limestone bedrock.

As described above, aquatic systems can exhibit significant diel chemical fluctuations due to biologic activity. These short-term fluctuations are driven by the daily photoperiod, which can influence instream temperature, pH and oxidative conditions, nutrient and carbon cycles, and dissolved gas gradients. With the potentially dynamic nature of DOC at any given site through the day, it is difficult to identify a meaningful spatial trend in DOC for the entire watershed based on samples collected at different sites and times during multi-day sampling events. There is not a clear correlation between total metals concentrations and DOC concentrations, as the mobility of metals appears to be influenced more by runoff and entrainment of sediment (TSS). A more refined monitoring program would be needed to identify the full scope of DOC fluctuations and any potential correlation between DOC and metals mobility.

Figure 3-7. Chloride concentrations for the Smith River and Sheep Creek, 2018-2019 events.

Figure 3-8. Sulfate concentrations for the Smith River and Sheep Creek, 2018-2019 events.

Figure 3-9. Sodium concentrations for the Smith River and Sheep Creek, 2018-2019 events.

Figure 3-10. Hardness concentrations for the Smith River and Sheep Creek, 2018-2019 events. In this case, total hardness is shown to represent trends for multivalent cations. Hardness is typically the sum of calcium and magnesium, although other cations at lower concentrations contribute to total hardness.

Figure 3-11. Dissolved organic carbon concentrations for the Smith River and Sheep Creek, 2018-2019 events.

Table 3-6. Major Ions and Organic Carbon- Smith River, all mainstem locations. Total fraction unless otherwise noted. Parameters and samples collected from May through October 2018 and May through October 2019. Locations and dates may extend beyond the complete samples for metals.

	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Bicarbonate, as HCO3 (mg/L)	Carbonate (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Hardness (mg/L)	Organic carbon, dissolved (mg/L)
Number of Samples	63	63	63	63	88	88	63	63	165	40
Number of Non-Detects	0			0		26		0		0
Number of J Flag Values	0			0		0		0		0
Minimum Value	30			4	111		1.4	15.5	111	2.2
Maximum Value	76	22		29	300	17	10.8	79.5	290	6.2
Mean Value	51	16		11	169		4.3	34.0	183	3.7

Table 3-7. Major Ions and Organic Carbon- Smith Tributaries, excluding Sheep Creek. Total fraction unless otherwise noted. Parameters and samples collected from May through October 2018 and May through October 2019. Locations and dates may extend beyond the complete samples for metals. Limited ions and no metals were sampled at these locations.

Table 3-9. Major Ions- White Sulphur Springs (Spa Motel), geothermal source that contributes to the South Fork of the Smith. Total fraction unless noted otherwise. Samples collected on 3/29/2011 as part of geothermal survey conducted by Montana Bureau of Mines and Geology (MBMG), from GWIC database.

3.3.6 Metals

Most metals occurred at low concentrations in the Smith River water samples, typically near or below the respective analytical method reporting limits (arsenic, cadmium, chromium, copper, lead, selenium, silver, and zinc). These concentrations are reported as "J-flag" values, when the number is between the reporting limit and the method detection limit. Although these are considered estimates rather than exact measurements, this information can sometimes help to identify general trends at low concentrations. Other metals like aluminum, barium, iron, manganese, and strontium may occur at slightly higher concentrations, but usually below numeric water quality standards. Trends observed for some of these metals can provide insight about potential loading from tributaries to the Smith River, anthropogenic sources, and/or weathering from different geologic regions.

The water quality results for total metals in the Smith River and Sheep Creek are shown in **Table 3-10** and **Table 3-11**, respectively. Note that the results for metals are reported in micrograms per liter (μg) , which is a thousand times less than the concentrations reported for major ions or other parameters in milligrams per liter (mg/L). The metals that occurred at very low concentrations with no discernible spatial or temporal trends are reported in these tables but are not discussed in detail in the following sections (arsenic, cadmium, chromium, selenium, silver).

Some of the higher metals concentrations measured during this study occurred during spring and early summer. This trend likely reflects a combination of metal-bearing suspended sediments and particles during high flow conditions and increased scouring, in addition to the dissolution of metals from sediments and bedrock during the infiltration of runoff. In early May 2019, the chronic aquatic life standard for dissolved aluminum (87 µg/L) was exceeded in one sample from Sheep Creek (163 µg/L) and one sample from the Smith River directly below the Sheep Creek confluence (142 µg/L). During three separate sampling events, the concentrations of total iron (a non-priority pollutant) in the Smith River exceeded the chronic aquatic life standard of 1,000 µg/L at the lower-most sampling point, directly upstream from the Missouri River confluence. These exceedances are summarized in **Table 3-10** and potential sources for a variety of metals are described further in the sections below.

Site Name	Waterbody	Map Site	Date	Parameter Result	Numeric Water	
		Label			Quality Standard	
Sheep Creek	Tributary	12T	5/10/2019	Aluminum, 163 µg/L	87 µg/L, Aquatic	
					Life- Chronic	
Smith River at	Smith River	13M	5/10/2019	Aluminum, 142 µg/L	87 µg/L, Aquatic	
Devil's Bridge					Life- Chronic	
Smith River	Smith River	27M	8/23/2018	Iron (total), $1,010 \mu g/L$	$1,000 \mu g/L$, Aquatic	
near Mouth					Life- Chronic	
Smith River	Smith River	27M	5/8/2019	Iron (total), $1,150 \mu g/L$	$1,000 \mu g/L$, Aquatic	
near Mouth					Life- Chronic	
Smith River	Smith River	27M	5/31/2019	Iron (total), 1,350 µg/L	$1,000 \mu g/L$, Aquatic	
near Mouth					Life- Chronic	
Smith River	Smith River	27M	6/11/2019	Iron (total), $1,190 \mu g/L$	$1,000 \mu g/L$, Aquatic	
near Mouth					Life- Chronic	

Table 3-10. Summary of numeric water quality standard exceedances (DEQ-7, 2019).

Aluminum

Dissolved aluminum concentrations in the Smith River were below the analytical method reporting limit (9 µg/L) for the upper reaches during all sampling events (**Figure 3-12, Figure 3-14**). During May 2019, the elevated dissolved aluminum concentration in Sheep Creek (163 µg/L) resulted in the closest downstream point on the Smith reaching 142 μ g/L, both samples exceeded the chronic aquatic life standard (87 μ g/L; **Table 3-10, Table 3-11, Table 3-12**). The dissolved aluminum concentrations continued to decrease in the middle portion of the watershed but remained elevated compared to the upper reaches. With a limited number of samples, it is not possible to precisely determine the full extent of elevated dissolved aluminum concentrations or the point along the Smith River where concentrations drop below the aquatic life numeric standard. In the subsequent sampling events during higher flow (late May to July 2019), a similar spike in dissolved aluminum occurred in the Smith River in response to contributions from Sheep Creek, followed by gradual downstream dilution. During baseflow conditions represented by the August through October samples (2018 and 2019), dissolved aluminum concentrations returned to levels near or below the analytical method reporting limit.

As discussed above, the Sheep Creek TMDL study considered potential sources contributing aluminum to Sheep Creek which included historical and existing mining, human caused land disturbances (other than mines), and natural background. The extent of mining disturbance in the watershed is limited (Section 2.2) and there are no direct discharges to surface water, thus the study concluded that historical (abandoned) mines and the one active mine within the Sheep Creek watershed (iron mine) are not considered sources of elevated aluminum loading. If other types of land disturbance resulted in increased erosion and metals mobility, there would likely be a positive relationship between high runoff and dissolved aluminum. The TMDL study concluded this was not the case and demonstrated that aluminum concentrations tended to fluctuate independent of TSS with some of the highest concentrations occurring when lower TSS values were observed. With "little to no linkage between aluminum and TSS loading and human related erosion activities in the watershed," the TMDL study considered other seasonal mechanisms for increased aluminum mobility (DEQ, 2020).

The results from this study are consistent with the observations in the TMDL study for Sheep Creek, where the higher concentrations in Sheep Creek and the Smith River occurred in late spring and early summer, but these did not always coincide with high flows or TSS values (**Figure 3-12**). The common thread identified in the TMDL study, and observed again here, is that high aluminum concentrations occur during the spring. This may be attributable to the runoff and infiltration originating from snow melt, which can have a slightly acidic pH between 5 and 6 s.u. (Utah State University, 2005). When snow melts rapidly, it may not percolate through the soil and undergo sufficient buffering or neutralization before weathering exposed geologic material or reaching the stream. Since the solubility of aluminum increases as pH decreases (Smith and Haines, 1995), there is an increase in the availability of aluminum in the water column which may be dispersed downstream, although there may not be a drastic change in pH to the stream.

Aluminum occurs naturally in aquatic ecosystems due to weathering of geologic materials containing feldspars (e.g. orthoclase, anorthite, albite), micas, and clay minerals. In natural systems, aluminum solubility is often controlled by gibbsite (aluminum hydroxide) and kaolinite (clay), depending on pH conditions. While aluminum is a common component of soil and rock-forming minerals, the geologic conditions and hydrothermal mineralization within the Sheep Creek drainage increase the potential sources of weathering and aluminum loading. The TMDL study noted other tributaries to Sheep Creek with elevated aluminum concentrations, sourced from natural weathering of areas not disturbed by human activities (Calf Creek, Moose Creek).

Figure 3-12. Aluminum concentrations (dissolved) vs. Total Suspended Solids (TSS) for the Smith River and Sheep Creek, 2018-2019 events. The analytical method reporting limit and detection limit are shown. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value (3 µg/L).

Barium

Total barium concentrations in the Smith and Sheep Creek were above the analytical method reporting limit (0.5 µg/L) for every sample from all sampling events, ranging between 66 and 108 µg/L (**Table 3-11, Table 3-12, Figure 3-13. Figure 3-15**). During May and June 2019, the barium concentration increased over the length of the Smith River watershed with notable increases at the lowermost sampling sites. The concentrations of barium in Sheep Creek (ranging from 70 to 118 µg/L) were similar to the Smith River during early months, but increased later in the year and exceeded the concentrations measured in the Smith River above or below the confluence. The barium load within Sheep Creek was greater than the adjacent upstream site on the Smith River for nearly all sampling events. This in turn increased the load at the site immediately downstream from the Sheep Creek confluence. Although the barium load typically increased for the remainder of the watershed and concentrations increased at the lowermost sites, the change in loads between downstream reaches was not to the magnitude observed at Sheep Creek.

Barium in water comes primarily from natural sources, being present in soil and a variety of rock types. The two most abundant minerals containing barium include barite (barium sulfate) and witherite (barium carbonate). Barium would not be expected to be very mobile because of the formation of water-insoluble compounds and its inability to form soluble complexes with humic and fulvic materials. However, the solubility of barium compounds increases as the pH level decreases (WHO, 1996) and some dissolved barium may be dispersed into groundwater or surface water. Soluble barium and suspended particulates can be transported great distances in rivers, and in the absence of removal mechanisms, the residence time of barium in aquatic systems could be several hundred years (Nielsen, E. et al, 2013). The concentration of barium ions in natural aquatic systems is limited by the presence of naturally occurring anions like sulfate, and potentially by adsorption of these ions onto metal oxides and hydroxides (Hem, 1959 in WHO, 1996).

Baseline data collected by the BBC Project provide insight about the geologic conditions affecting the water quality of Sheep Creek and its tributaries. Geologic sampling in the area indicates an abundance of barite in the Precambrian Newland Formation, which is a carbonate-rich shale that occurs across a portion of the Sheep Creek drainage (Tintina, 2017). In Little Sheep Creek, Sheep Creek below the BBC Project, Coon Creek, and Black Butte Creek, barium concentrations ranged from 83 to 168 µg/L. The downstream Sheep Creek tributaries, like Calf Creek, Cameron Creek, and Moose Creek had barium concentrations ranging from 49 to 98 µg/L. Baseline groundwater sampling conducted for the project measured barium in all local aquifer units near the proposed underground mine, with some natural concentrations greater than the human health standard $(1,000 \mu g/L)$ within the unconsolidated overburden and mineralized bedrock aquifers.

The relationships between total and dissolved barium concentrations and TSS for Sheep Creek and Smith River are shown in **Figure 3-13**. The separation between total and dissolved concentrations for a particular sample indicates the fraction of barium that occurs as a non-dissolved particle (>0.45 µm), which may be associated with sediment transport. Although the separation between dissolved and total concentrations seems to increase for the highest TSS values, the total concentrations are within a similar range as the samples with low TSS. Many of the highest barium concentrations measured in this study occurred in Sheep Creek, with little difference between total and dissolved concentrations. This indicates that barium occurs primarily in the dissolved phase and is not directly associated with increased flow and elevated TSS values, similar to the aluminum dynamics described above. However, the concentrations increased later in the year when the effects from slightly acidic snow melt infiltration would be less pronounced. This indicates that other mechanisms control the weathering and mobilization of barium in the Sheep Creek watershed through the year, which could include pH-driven dissolution into groundwater within sulfide mineralized zones, equilibria with sulfate and carbonate species, adsorption to and from other mineral surfaces, and/or greater relative contributions to the stream from groundwater during baseflow conditions.

Figure 3-13. Barium concentrations (dissolved) vs. Total Suspended Solids (TSS) for the Smith River and Sheep Creek, 2018-2019 events.

Figure 3-14. Aluminum concentrations (dissolved) for the Smith River and Sheep Creek, 2018-2019 events. Note the logarithmic scale for y-axis. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath.

Figure 3-15. Barium concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. All total barium results were above the reporting limit (0.5 µg/L).

Iron

Total iron concentrations in the Smith River and Sheep Creek were above the analytical method reporting limit (20 µg/L) for all but one sample (**Table 3-11, Table 3-12, Figure 3-16, Figure 3-17**). During May and June 2019, the total iron concentration increased between the upper reaches of the Smith River, likely reflecting high flows and elevated TSS values. The total iron concentrations measured in Sheep Creek at that time are similar or slightly less than the Smith River site upstream of the confluence. The total concentrations for both streams decrease under baseflow conditions later in the year, with the concentrations in Sheep Creek being greater in some examples. Comparing the sites directly above and below the Sheep Creek confluence shows that this tributary increases the iron load of the Smith River during nearly all months (**Appendix A**).

The relationships between total and dissolved iron concentrations and TSS for Sheep Creek and Smith River are shown in **Figure 3-16**. The samples from the Smith River had higher concentrations of total iron than dissolved iron, with an average total iron to dissolved iron ratio (Fe-TR:Fe-D) of 29:1. Sheep Creek samples were also dominated by total iron concentrations, but there was a higher relative concentration of dissolved iron in Sheep Creek, with an average Fe-TR:Fe-D ratio of 8:1. The majority of total iron in both streams occurs as a non-dissolved particle $(>0.45 \mu m)$ and the concentrations increase directly with increasing TSS. The mobility of iron within streams can be influenced by physical actions like erosion and sediment entrainment, as well as geochemical processes like the precipitation and adsorptive properties of iron oxyhydroxides, further influenced by changes to pH and oxidation conditions from biological processes.

Iron is listed as a nonpriority pollutant (DEQ-7, 2019), but the exceedances of the chronic aquatic life standard (1,000 µg/L) at these lower sites are summarized in **Table 3-10**. Although the numeric water quality standard was not exceeded in other months, there were notable increases in total iron in the Smith River within approximately 23 miles of the Missouri confluence during most sampling events. This correlates with the spatial changes observed in TSS, sulfate, and total manganese concentrations for the lower reaches of the Smith River, in addition to slight increases in low-concentration trace metals like copper, lead, and zinc. The total iron concentrations likely reflect a combination of entrainment of ironbearing sediment from land disturbance that may be related to agriculture, land development, or mining. In addition to potential contributions from historical coal mine discharge, total iron sources could include the *in-situ* oxidation of shallow, iron sulfide-bearing coal deposits or other iron-bearing formations, and/or geochemical cycling within the benthic sediment and water column. These mechanisms also likely control the slight increases observed in the dissolved iron concentrations in the lowermost Smith River sites.

The dissolved iron concentrations in the Smith River and Sheep Creek follow slightly different trends than the totals (**Figure 3-17 and Figure 3-18**). The concentrations in upper reaches of the Smith River are below or near the reporting limit (20 μ g/L) for all events and flow conditions. The dissolved iron concentrations in Sheep Creek and the lower reaches of the Smith River were significantly higher during the May 2019 events and declined in following months. The dissolved concentrations in Sheep Creek remained higher than nearly all other samples from downstream Smith River locations.

Similar to the dynamics observed for aluminum and barium, the solubility and mobility of iron increases with decreasing pH. Within the Sheep Creek watershed, iron is likely influenced by infiltration of snow melt and the weathering of geologic material at shallow depth. Some places in the watershed contain an oxidized iron capping layer (gossan) at the surface (Tintina, 2017). Given the age of the sulfide mineralization that formed along a sea floor setting (approximately 1.4 billion years old), the occurrence of gossan in this region indicates the uplift, exposure, and natural weathering reactions of sulfide minerals

over vast geologic time scales. This oxidation would have produced acidity and mobilized metals and other elements over long periods, contributing to the flux of mineral precipitates and sediments that influence the baseline characteristics of the watershed. The limited oxidation of deep sulfide mineralization may mobilize iron to groundwater in some places, but the trends for other oxidation-related constituents like sulfate, other trace metals, and pH do not suggest that this is a significant source to Sheep Creek.

Figure 3-16. Iron concentrations (total and dissolved) vs. Total Suspended Solids (TSS) for the Smith River and Sheep Creek, 2018-2019 events. The analytical method reporting limit is shown, with points below this line reflecting the J-flag results.

Figure 3-17. Iron concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Note the logarithmic scale for y-axis. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath. All total iron results were above the detection limit, which ranged from 2 to 6 µg/L between analyses.

Figure 3-18. Iron concentrations (dissolved) for the Smith River and Sheep Creek, 2018-2019 events. Note the logarithmic scale for y-axis. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath (range from 2 to 6 µg/L).

Manganese

Total manganese concentrations in the Smith and Sheep Creek were above the analytical method reporting limit (1 µg/L) for all samples (**Table 3-11, Table 3-12, Figure 3-19, Figure 3-21**). During most sampling events, the total concentration increased between the upper reaches of the Smith River, reflecting sources that persist beyond periods of high flows and TSS values. The total concentrations measured in Sheep Creek are consistently lower than the Smith River at the nearest upstream site. The effects of dilution and decreasing concentrations occurred through the middle portion of the watershed, and a significant decrease in the load in this area for some sampling events may indicate precipitation, adsorption, or other removal mechanism. With a change in geologic conditions and increased land disturbance near the lowermost sampling sites, there are notable increases in manganese for almost every sampling event. There was a slight decrease in the magnitude of the range of total concentrations from high flow to baseflow months, but this temporal trend is less pronounced than what occurs for some other parameters.

The dissolved manganese concentrations in the Smith River and Sheep Creek follow slightly different trends than total manganese concentrations (**Figure 3-22**). The dissolved concentrations decreased between the upper reaches of the Smith River while total manganese increased, with a few exceptions during baseflow conditions in later months. Increases in dissolved manganese were also observed for the lowermost Smith River sites, although the magnitude is not as great as the changes in total concentrations. Some of the mechanisms that affect iron mobility also influence manganese, particularly in the lower reaches where changes in TSS, sulfate, and trace metals are also observed.

The dissolved manganese in Sheep Creek was consistently below the concentrations measured in the Smith, although concentrations increased slightly in later months, which may reflect reduced dilution from flow and/or more relative input from groundwater. The relationships between total and dissolved manganese concentrations and TSS for Sheep Creek and Smith River are shown in **Figure 3-19**. For most samples, the dissolved fraction is a minor component of the total concentration. Some of the higher dissolved concentrations within the Smith River occurred in samples with relatively low TSS. The correlation between TSS and total concentration is not as clear as other parameters like iron and lead, indicating there are other processes that influence manganese mobility within the streams.

The principal common minerals of manganese include oxides and oxyhydroxides (pyrolusite, psilomelane, manganite) and carbonate (rhodochrosite) (Hem, 1963a). Like iron oxyhydroxides, some manganese compounds may form precipitates within benthic sediment and the mineral surfaces are common sites for adsorption of other constituents in the aquatic system. Manganese often coprecipitates with ferric hydroxide when the pH is greater than 6.7, although manganese is generally more soluble than iron under the Eh-pH conditions common in surface water (Hem, 1963b). Solubility generally increases with decreasing pH, but the availability of manganese in aquatic systems is strongly influenced by chemical equilibria involving Mn^{+2} , Mn⁺³, and Mn^{+4} species. Similar to iron, these species can be affected by changes in pH and oxidation-reduction conditions, including biologic activity at a very small/isolated scale. Although precipitates may form under favorable kinetic conditions, manganese can also form soluble complexes with bicarbonate and sulfate, increasing its mobility within surface water (Hem, 1963a).

The relatively low concentrations of manganese in Sheep Creek are consistent between sampling events, indicating that the weathering cycles that mobilize other metals have less effect on manganese and/or there is less abundance of manganese within the geologic materials in that watershed.

Figure 3-19. Manganese concentrations (total and dissolved) vs. Total Suspended Solids (TSS) for the Smith River and Sheep Creek, 2018-2019 events. The analytical method reporting limit is shown.

Lead

Total lead concentrations in the Smith River and Sheep Creek were relatively low, with all results less than or equal to 1 µg/L (**Table 3-11, Table 3-12, Figure 3-20 and Figure 3-23**). Many of the higher concentrations within the Smith River and Sheep Creek were measured during sampling events with high flow and TSS values. With a few exceptions, most of the samples from later months had concentrations near or below the analytical reporting limit of 0.3 µg/L, but above the detection limit of 0.04 µg/L (J-flag values).

During most sampling events, the total concentration increased between the upper reaches of the Smith River, reflecting tributary sources in this portion of the watershed. The total concentrations measured in Sheep Creek are consistently lower than the Smith at the nearest upstream site, and some degree of dilution and decreasing concentrations occurred through the middle portion of the watershed below the Sheep Creek confluence. With a change in geologic conditions and increased land disturbance near the lowermost sites, there were increases observed in lead for almost every sampling event, although the magnitude of this change is not as pronounced as other metals like iron and manganese.

The relationships between total and dissolved lead concentrations and TSS for Sheep Creek and Smith River are shown in **Figure 3-20**. Dissolved lead occurred at very low concentrations in Sheep Creek and the Smith River, and the total concentrations primarily reflect the occurrence of lead as non-dissolved particles (>0.45 µm). In addition to adsorption processes on mineral and organic surfaces, the solubility of lead can be controlled primarily by chemical equilibria with carbonate, orthophosphate, and sulfate, and the potential formation of soluble complexes (Jurgens et al, 2019). The few dissolved concentrations that were reported as J-flag values occurred across all reaches of the Smith and Sheep Creek during the

May and August 2019 sampling events, ranging from 0.04 to 0.12 µg/L with no clear spatial trend (no figure provided). The highest concentrations of total lead correspond directly to high TSS values (**Figure 3-20**). Although some lead may be mobilized through geochemical processes and the dissolution of minerals at different locations in the watershed, the data suggest that physical action through erosion and sediment transport is the most significant source of lead to the Smith River.

Figure 3-20. Lead concentrations (total and dissolved) vs. Total Suspended Solids (TSS) for the Smith River and Sheep Creek, 2018-2019 events. The analytical method reporting limit and detection limit are shown. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value (0.04 µg/L).

Figure 3-21. Manganese concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath. All total manganese results were above the reporting limit (1 µg/L).

Figure 3-22. Manganese concentrations (dissolved) for the Smith River and Sheep Creek, 2018-2019 events. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath. All dissolved manganese results were above the reporting limit (1 µg/L).

Figure 3-23. Lead concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Note the logarithmic scale for y-axis. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath (0.04 µg/L).

Copper

Total copper concentrations in the Smith River and Sheep Creek were relatively low, with all results less than or equal to 2 µg/L (**Table 3-11, Table 3-12, Figure 3-25**). Many of the higher concentrations within the two streams were measured during sampling events with high flow and TSS values. With a few exceptions, most of the samples from later months had concentrations near or below the analytical reporting limit of 1 µg/L, but above the range of detection limits from 0.1 to 0.3 µg/L (J-flag values).

During most sampling events, the total concentration increased slightly between the upper reaches of the Smith, which may reflect tributary sources in this portion of the watershed. The total concentrations measured in Sheep Creek were higher during high-flow periods and then decreased in later months to concentrations below the nearest upstream site on the Smith River. Load estimates from the sites upstream and downstream from the Sheep Creek confluence indicate a slight increase from Sheep Creek contributions. This aligns with the benthic sediment results, showing that Sheep Creek and Calf Creek had the highest copper concentrations in the study (**Table 3-14**). This sediment composition likely reflects weathering of the various copper minerals (e.g. chalcopyrite, tennantite) that are known to occur within the mineralized zones of the Sheep Creek watershed (Tintina, 2017).

Copper concentrations remained steady or decreased slightly through the middle portion of the Smith River watershed, but then increased at the lowermost sites for most sampling events. This may be related to the increases observed in other metals and parameters, whether due to increased sediment inputs from human disturbance (agriculture and mining) and/or due to adsorption or other geochemical processes that may mobilize constituents present within benthic sediment.

Similar to other transition metals like lead and zinc, copper has relatively low solubility in oxidizing conditions with neutral to slightly alkaline pH conditions. These metals may form insoluble carbonate, oxide, or hydroxide compounds. Copper may be adsorbed to iron or manganese oxyhydroxide surfaces within benthic sediment. The mobility of adsorbed copper can be affected by changes to pH or oxidative conditions. Copper also forms soluble complexes with dissolved organic carbon more readily than other transition metals (Drever, 2002). Given the low total copper concentrations and relatively low carbon concentrations, the formation of copper complexes does not appear to be a significant process for mobilizing copper within the Smith River or Sheep Creek.

Strontium

Total strontium concentrations in the Smith River and Sheep Creek were above the analytical method reporting limit (10 µg/L) for every sample from all sampling events, ranging from 160 to 530 µg/L and from 60 to 120 µg/L, for the two respective streams (**Table 3-11, Table 3-12, Figure 3-24, Figure 3-26**). The temporal trends observed for strontium track closely with calcium, although calcium occurs at concentrations that are orders of magnitude greater. Likely due to seasonal runoff and dilution, the range of concentrations during high-flow periods are slightly less than those observed in later months. Given that calcium and strontium are alkaline earth metals with similar chemical properties (Nitzche, 2022), some of the geologic sources and mobilization mechanisms within the watershed are likely the same.

Upper portions of the watershed exhibit elevated strontium concentrations, likely resulting from dilution of the geothermal system feeding the South Fork of the Smith River, which had a dissolved concentration of 1,935 µg/L (**Table 3-13**). The upper reaches of the Smith River exhibited some of the highest strontium concentrations followed by gradual dilution, while the effects from the low concentrations in Sheep Creek were significant in the closest downstream sampling site on the Smith River. Concentrations increased through the remainder of the watershed, likely sourced from the carbonate rocks and potential groundwater inputs that occur within the middle and lower portions of the watershed.

The relationships between total and dissolved strontium concentrations and TSS for Sheep Creek and Smith River are shown in **Figure 3-24**. There is a small difference between the total and dissolved concentrations, indicating the majority of mobile strontium in the watershed is in the dissolved phase, even for the sampling events with high flow and elevated TSS values.

Baseline data collected by the BBC Project provide insight about the geologic conditions affecting the water quality of Sheep Creek and its tributaries. Geologic sampling in the area indicates an abundance of minerals like celestine (SrSO₄) and strontianite (SrCO₃) in the Precambrian Newland Formation, which is a carbonate-rich shale that occurs across a portion of the Sheep Creek drainage (Tintina, 2017). Strontium and barium were measured consistently in previous Sheep Creek monitoring and concentrations appear to be greater in the upper portions of the drainage than in the downstream tributaries. In Little Sheep Creek, Sheep Creek below the BBC Project, Coon Creek, and Black Butte Creek, strontium concentrations ranged from 78 to 147 µg/L. The downstream Sheep Creek tributaries, like Calf Creek, Cameron Creek, and Moose Creek had strontium concentrations ranging from 20 to 50 µg/L. Baseline groundwater sampling conducted for the BBC Project measured strontium in all local aquifer units near the proposed underground mine, with some natural concentrations greater than the human health standard (4,000 µg/L) within the unconsolidated overburden and mineralized bedrock aquifers. Unlike barium, the occurrence of strontium at such concentrations within the Sheep Creek watershed does not result in a significant load to the Smith River. The mobility of strontium may be constrained by solubility and weathering of specific minerals within the Sheep Creek area, as well as equilibria with carbonate or sulfate once dissolved.

Figure 3-24. Strontium concentrations (total and dissolved) vs. Total Suspended Solids (TSS) for the Smith River and Sheep Creek, 2018-2019 events.

Zinc

Total zinc concentrations in the Smith River and Sheep Creek were relatively low, with all results less than or equal to the analytical reporting limit of 8 µg/L (**Table 3-11, Table 3-12, Figure 3-27**). Many of the higher concentrations within the Smith River and Sheep Creek were measured during sampling events with high flow and TSS values. With a few exceptions, most of the samples from later months had concentrations near or below the range of method detection limits $(1 to 4 \mu g/L)$.

During some sampling events, the total concentration increased between the upper reaches of the Smith River, which may reflect tributary sources in this portion of the watershed. The total concentrations measured in Sheep Creek were consistently lower or equal to the Smith at the nearest upstream site. Based on load estimates (**Appendix A**), there was typically an increase in zinc between the Smith River sites upstream and downstream from the Sheep Creek confluence. However, the contribution from Sheep Creek is minor and it may be that Eagle Creek is a source of zinc to the Devil's Bridge site on the Smith River. For most sampling events, there was a slight increase observed for concentration and load in the lowermost Smith River sites. This may be related to the increases observed in other metals and parameters, whether due to increased sediment inputs from human disturbance (agriculture and mining) and/or due to adsorption or other geochemical processes that may mobilize constituents present within benthic sediment (Section 3.4).

Similar to other transition metals like lead and copper, zinc has relatively low solubility in oxidizing conditions with neutral to slightly alkaline pH conditions. These metals may form insoluble carbonate, oxide, or hydroxide compounds. Zinc may be adsorbed to iron or manganese oxyhydroxide surfaces within benthic sediment, and its mobility can then be affected by changes to pH or oxidative conditions. Zinc may also form soluble complexes with dissolved organic carbon, but this is typically only prevalent when carbon concentrations are relatively high (Drever, 2002). Given the low total zinc concentrations and relatively low carbon concentrations, this does not appear to be a significant process for mobilizing zinc within the Smith River or Sheep Creek.

Figure 3-25. Copper concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath (range from 0.1 to 0.3 µg/L).

Figure 3-26. Strontium concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. All total strontium results were above the reporting limit (10 µg/L).

Figure 3-27. Zinc concentrations (total) for the Smith River and Sheep Creek, 2018-2019 events. Numeric standards are shown on the graph if applicable, in addition to the analytical method reporting limit and detection limit. Points shown between these analytical limits reflect the J-flag results, while the points below the detection limit are shown at half of that respective value to depict a continuous flowpath (range from 1 to 4 µg/L).

	Aluminum, dissolved	Arsenic $(\mu g/L)$	Barium $(\mu g/L)$	Cadmium $(\mu g/L)$	Chromium $(\mu g/L)$	Copper $(\mu g/L)$	Iron $(\mu g/L)$	Lead $(\mu g/L)$	Manganese $(\mu g/L)$	Selenium $(\mu g/L)$	Silver $(\mu g/L)$	Strontium $(\mu g/L)$	Zinc $(\mu g/L)$
	$(\mu g/L)$												
Number of Samples	10	10	10	10	10	10	10	10	10	10	10	10	10
Number of Non-Detects	4	0	$\mathbf{0}$	9		0	$\mathbf{0}$	$\overline{2}$	0	3	$\overline{7}$	$\mathbf{0}$	
Number of J Flag Values		9	$\mathbf 0$	Ω	8	8	$\mathbf{1}$	7	0	7	3	$\mathbf{0}$	9
Minimum Value	5.	0.6	70.5	0.10	0.2	0.3	30	0.04	6	0.07	0.01	60	$\overline{2}$
Maximum Value	163	1.0	118.0	0.10	1.0	2.0	840	0.30	30	0.21	0.02	120	4
Mean Value	51	0.8	100.2	0.10	0.6	0.8	282	0.16	16	0.11	0.01	100	3
Number of Acute AQL Exceedances	$\mathbf{0}$	0	NA	$\mathbf{0}$	0	0	$\mathbf{0}$	0	NA	Ω	$\mathbf 0$	NA	Ω
Number of Chronic AOL Exceedances	1	0	NA	Ω	Ω	0	0	0	NA	Ω	NA	NA	Ω
Number of Human Health Exceedances	NA	0	$\mathbf 0$	$\mathbf{0}$	0	0	NA	Ω	NA	Ω	Ω	$\mathbf{0}$	Ω

Table 3-12. Metals- Sheep Creek near Smith River confluence. Total fraction unless otherwise noted. Samples collected from August through October 2018 and May through October 2019. Load estimates and comparisons were not prepared in Appendix A for cadmium or silver due to lack of sufficient data.

Table 3-13. Metals- White Sulphur Springs (Spa Motel), geothermal source that contributes to the South Fork of the Smith. Dissolved fraction unless noted otherwise. Samples collected on 3/29/2011 as part of geothermal survey conducted by Montana Bureau of Mines and Geology (MBMG), from GWIC database.

3.4 BENTHIC SEDIMENT RESULTS AND DISCUSSION

Samples of benthic (streambed) sediments were collected in August 2018 at some of the sites sampled for water quality and the results are displayed in **Table 3-14**. The list of parameters is provided in **Table 1- 2**. Spatial trends for metal concentrations in sediments are shown in **Figure 3-28, Figure 3-29,** and **Figure 3-30**. Similar to trends in water quality parameters, the slight increases in some metals (arsenic, cadmium, copper, iron, and zinc) at the lowermost Smith River site may be reflective of land disturbance related to agriculture, mining, and/or weathering and erosion of surrounding geologic material. Sediment samples were only collected during one event, so temporal trends are not discussed. Some of the total recoverable water samples from high-flow periods are likely representative of the seasonal water quality influences from the entrainment of sediment.

Arsenic concentrations are between 3.19 and 4.19 μ g/g (ppm) in upper portions of the watershed, with an increase to 4.63 μ g/g in the lowermost sample site. Higher concentrations were measured in Sheep Creek as well as the Calf Creek reference site (6.21 and 4.94 µg/g, respectively), which likely reflects the geologic region and weathering of mineralized areas within these watersheds. The Sheep Creek TMDL report considered Calf Creek to be a "reference" site because it is in an area of the Sheep Creek watershed that is mostly undisturbed by human activities (DEQ, 2020). All samples were greater than the background value provided by NOAA (1.1 μ g/g). Similar to trends in other parameters, the slight increase in arsenic at the lowermost Smith River site may be reflective of land disturbance related to agriculture, mining, and/or weathering and erosion of surrounding geologic material.

Mercury concentrations were consistently below the analytical reporting limit in all Smith River samples (0.02 µg/g, J-flag) and a slightly higher concentration was measured in Sheep Creek (0.05 µg/g, J-flag). The reference sample from Calf Creek had the only mercury concentration that was above the reporting limit $(0.11 \mu g/g)$ representing a background source that does not include human activity. All samples were greater than the background range provided by NOAA but this may be due in part to method reporting limits and may not be indicative of actual trends in mercury concentrations.

Cadmium concentrations were very similar among all Smith River samples (0.20 to 0.29 μ g/g) except for the two lowermost samples (0.42 and 0.50 μ g/g). The Sheep Creek sample (0.22 μ g/g) falls within a similar range as the Smith River, but Calf Creek is slightly higher (0.318 µg/g). These sediment concentrations do not seem to influence water quality in the streams, with the majority of total cadmium concentrations being below detection limits (<0.03 µg/L). Only a few water samples from the Smith River had cadmium concentrations at detectable concentrations (0.03 and 0.04 μ g/L), primarily at the lowermost sampling point, above the Missouri confluence.

Most of the Smith River sediment samples had chromium concentrations within the background range $(10.4 \text{ to } 13.9 \text{ µg/g})$ and the Sheep Creek and Calf Creek samples had approximately twice the concentrations measured in the Smith (25.3 and 24.9 µg/g, respectively). As shown in **Table 3-11**, the water quality samples indicate that the majority of chromium concentrations were below reporting limits (J-flag). Slight increases in chromium were observed in the sediment samples from lower reaches compared to upper reaches, but the data indicate the sediment concentrations generally have little influence on water quality.

Copper concentrations in the Smith River sediments (12.9 to 16.2 µg/g) were within the background range from NOAA, with a generally increasing trend from upstream to downstream and the highest concentration measured at the lowermost site. The highest copper concentrations in the study were measured in Sheep Creek (17.3 µg/g) and Calf Creek (24.9 µg/g) sediments, approaching the upper limit of the range of background concentrations from, NOAA (10.0 to 25.0 µg/g). This sediment composition likely reflects weathering of the various copper minerals (e.g. chalcopyrite, tennantite) that are known to occur within the mineralized zones of the Sheep Creek watershed (Tintina, 2017).

Lead concentrations in the Smith River sediments were within the background range from NOAA, ranging from 10.5 and 14.6 µg/g. Unlike other metals, there does not appear to be an increasing trend with stream length and the lowest concentration was measured at the lowermost site. The water quality results indicate a direct connection between total lead concentrations and TSS values, so slight increases in total lead concentrations (like lower Smith River sites) may result from other sources of non-dissolved lead other than entrainment of local benthic sediment. The lead concentrations measured in sediments from Sheep Creek (11.9 μ g/g) and Calf Creek (12.6 μ g/g) are within the range observed in the Smith River, unlike the other metals that occur at higher relative concentrations in those tributaries.

Iron concentrations in the Smith River sediments were within the background range from NOAA, although below the analytical reporting limit for each sample (J-flag). Concentrations gradually increase from 10,400 to 13,000 µg/g over the length of the watershed. Tributaries like Sheep Creek and Calf Creek have higher concentrations than any of the Smith River locations (16,500 and 19,600 µg/g, respectively), likely a result from the weathering of geologic material in this area. As noted in the water quality results, the total concentrations of iron in Sheep Creek were similar to the Smith River in some examples, however the dissolved iron in Sheep Creek is consistently higher than the nearest Smith River samples during baseflow conditions. This may indicate different mechanisms for mineral dissolution and iron mobility in this watershed, rather than simply sediment particle entrainment.

Zinc concentrations in Smith River sediments were greater than the background range at all sampling locations. A generally increasing trend is noted over the length of the watershed (ranging 48.3 to 60.7 µg/g), although the increase is less pronounced than some other parameters. The sediments in Sheep Creek and Calf Creek had zinc concentrations that were slightly higher than those measured in the Smith River (63.2 and 66.5 µg/g, respectively). However, the concentrations and loads for Sheep Creek are consistently lower or equal to the nearest upstream site on the Smith River, so this tributary does not appear to be a significant source of mobile zinc. As noted previously for water quality samples, the concentrations of total zinc in the Smith River and in Sheep Creek are consistently below the analytical reporting limit, but the J-flag data indicate increasing zinc concentrations at the lowermost sites on the Smith River.

Table 3-14. Comparison of metals concentrations in streambed sediments to "background" values from NOAA, 2008 (from Buchman, 1999). All values are shown in concentrations units of µg/g (ppm) and all results are depicted in Figure 3-28, Figure 3-29, and Figure 3-30. Values with a "J" indicate a result below the analytical method reporting limit but above the detection limit. With a few exceptions, the majority of sediment metal concentrations are within the background ranges established by NOAA. Calf Creek is considered to be a reference site because this tributary in the Sheep Creek watershed is mostly undisturbed by human activities.

Figure 3-28. Concentrations of arsenic, cadmium, and mercury within benthic sediment samples collected from the Smith River, Sheep Creek, and Calf Creek during 2018. Note the logarithmic scale on the vertical axis. All mercury data were reported as J-flag results except for the Calf Creek sample.

Figure 3-29. Concentrations of chromium, copper, and lead within benthic sediment samples collected from the Smith River, Sheep Creek, and Calf Creek during 2018.

Figure 3-30. Concentrations of zinc and iron within benthic sediment samples collected from the Smith River, Sheep Creek, and Calf Creek during 2018. Note that zinc is on the left vertical axis and iron is on the right vertical axis. All iron data were reported as J-flag results except for the Calf Creek sample.

4.0 DATA VALIDATION AND STATISTICAL ANALYSIS

As described in the 2018 and 2019 Metals Monitoring SAP documents, data quality control (QC) included procedures and protocols for measurements in the field and laboratory. Data QC is also performed by the Water Quality Planning Bureau's data management and QC systems prior to release to project staff for use.

Sampling events included the collection of field duplicates and field blanks, which were submitted to the analytical laboratory for the water quality parameter list shown in **Table 1-3**. Field blanks consisted of the appropriate analytical-grade deionized water provided by the laboratory transported to the field and poured off into a prepared sample container and preserved in the field. The blanks are treated the same as grab samples taken from the site. Field duplicates consisted of two independent samples collected at the same time and location under the same field conditions. Specific instructions for collecting field blanks and field duplicates are further described in the WQPB Field Procedures Manual for Water Quality Assessment Monitoring (DEQ, 2012). The accuracy and precision of field instruments are verified by certified control standards (e.g. NIST, USGS) and the duplicate measurements of standards, in addition to calibration prior to each field trip. Analytical laboratories prepared and analyzed the samples in accordance with the chain-of-custody forms and the methods in **Table 1-3**, and additional laboratory QC data are submitted with the water quality results. The results for field blanks and field duplicates are shown for the Smith River and Sheep Creek within **Table 4-1, Table 4-2, Table 4-3, and Table 4-4**.

There were few deviations from the 2018 and 2019 Metals Monitoring SAP documents. There were a few cases where site access, safety, or weather conditions prevented sampling from taking place, examples include:

- Smith River at Camp Baker (11M)- no metals sample or flow measured in July 2019;
- Smith River at Castle Bar Road (17M)- no flow measured for any events, no metals sample in October 2018, early May 2019, August 2019, and October 2019.
- Sheep Creek (12T)- no flow measurements from September 2018 through June 2019.
- Smith River near Mouth (27M)- no flow measurements except for July 2019 and October 2019.

Although this limits some of the data interpretation for particular sampling events, it does not interfere with the general assessment of baseline conditions and trends.

	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Bicarbonate, as HCO3 (mg/L)	CI (mg/L)	SO4 (mg/L)	Alkalinity, as CaCO ₃ (mg/L)	Hardness (mg/L)	TSS (mg/L)	Organic carbon, dissolved (mg/L)
Number of Samples	11	11	11	11	17	11	11	23	23	23	8
Number of Non-Detects		9	10	11	15	11	9	18	23	18	8
Number of J Flag Values	4			0	0	0	2	0	0	5	0
Minimum Concentration	0.09	0.01	0.07	0		0	0.02		0	0.4	0
Maximum Concentration	0.48	0.01	0.07	0		0	0.02	3	0	0.8	0
Average Concentration	0.21	0.01	0.07	0		0	0.02	2.4	0	0.6	0

Table 4-1. Blank samples, major ion and parameter concentrations. Total recoverable fraction unless noted.

Table 4-2. Blank samples, metal concentrations. Total recoverable fraction unless noted.

	Al, dissolved (ug/L)	As (ug/L)	Ba (ug/L)	Cd (ug/L)	Cr (ug/L)	Cu (ug/L)	Fe (ug/L)	Pb (ug/L)	Mn (ug/L)	Hg (ug/L)	Se (ug/L)	Ag (ug/L)	Sr (ug/L,	Zn (ug/L)
Number of Samples	11	11	11	11	11	11	11	11	11	0	11	11	11	11
Number of Non-Detects	11		9	11			9	11	11	0	8	10	11	
Number of J Flag Values	0	4			4	4		0	0	0	3		0	8
Minimum Concentration	0	0.06	0.13	0	0.2	0.2	6	0	0	0	0.05	0.1	0	
Maximum Concentration	0	0.16	0.24	Ω	0.4		14	0		0	0.11	0.1	Ω	
Average Concentration		0.09	0.19		0.3	0.4	10	0		0	0.07	0.1		2.3

	Ca (mg/L)	Mg (mg/L)	К (mg/L)	Na (mg/L)	Bicarbonate, as HCO3 (mg/L)	CI (mg/L)	SO4 (mg/L)	Alkalinity, as CaCO3 (mg/L)	Hardness (mg/L)	TSS (mg/L)	Organic carbon, dissolved (mg/L)
Number of Replicate Pairs	11	11	11	11	11	11	28	30	30	9	24
Pairs with One or Both Non-Detects	0	0	0	0	0	0	0	0	0	0	0
Pairs with One or Both J Flag Values	0	0	0	0	0	0	4	0	0	0	0
Minimum % Error	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maximum % Error	5.6	5.3	33.3	11.1	1.2	0.9	64.9	5.1	4.7	12.8	6.3
Average % Error	1.7	0.5	6.1	2.7	0.3	0.5	9.9	0.5	1.2	2.9	0.8

Table 4-3. Replicate samples, major ion and parameter concentrations. Total recoverable fraction unless noted.

Table 4-4. Replicate samples, metal concentrations. Total recoverable fraction unless noted.

5.0 CONCLUSIONS

The Smith River is a calcium-magnesium-bicarbonate type water with moderately high alkalinity (100 to 272 mg CaCO₃/L) and sufficient buffering capacity to maintain pH levels between 7.68 and 8.87 (standard unit- s.u.) in all mainstem reaches during the period of this study. The concentrations of major ions consistently decrease between the upper reaches and the final sampling point at the confluence with the Missouri River (bicarbonate, calcium, chloride, magnesium, sodium, sulfate). This trend reflects inputs from surface water tributaries and exchanges with groundwater systems over the approximate 125-mile length of the river. With a few exceptions, these inputs typically dilute the ionic signatures of the upstream Smith mainstem flow and the headwater sources, particularly the geothermal water influencing the South Fork of the Smith. In addition to spatial changes and tributary dilution, concentrations of major ions like calcium, magnesium, sodium, sulfate, and bicarbonate undergo dilution during seasonal high-flow periods in the spring and then tend to increase when flows return to base conditions in late summer and fall.

However, the high-flow periods also increase erosion and scouring, which increases the concentrations of total suspended solids (TSS) and total metals within the river for a short time period, particularly aluminum, iron, and manganese. The dissolved fraction of these metals may also occur at relatively elevated concentrations due to weathering of sediments and rocks by slightly acidic snow melt runoff in the spring. Most other metals occur at low concentrations in the Smith River, typically near or below the respective analytical method reporting limits (arsenic, cadmium, chromium, copper, lead, selenium, silver, and zinc). Other metals like aluminum, barium, iron, manganese, and strontium occur at slightly higher concentrations during periods of low flow, but often below numeric water quality standards. Spatial trends observed for some of these metals provide insight about potential loading from tributaries to the Smith, anthropogenic sources, and/or weathering from different geologic regions.

Preliminary assessment of metals data from 2013 to 2023 shows an exceedance rate of 1.96% for the chronic aquatic life/fishes standard for dissolved aluminum and 1.47% for the chronic aquatic life/fishes standard for iron for the North and South Forks of the Smith River to its confluence with Hound Creek (MT41J001_010). Metals data for this assessment unit was below the allowable 10% exceedance rate for both acute and chronic aquatic life standards. Whereas, for that same ten-year timeframe, preliminary assessment of metals data for the assessment unit that encompasses the Smith River, from Hound Creek to its mouth at the Missouri River (MT41J001_020), exhibited an exceedance rate of 13.51% for the chronic aquatic life/fishes standard for iron, which is greater than the allowed 10% exceedance rate. Montana will list this segment of the Smith River for Iron as a category 5 listing in the next Integrated Report. A category 5 listing means one or more applicable beneficial uses have been assessed as being impaired or threatened, and a TMDL is required to address the factors causing the impairment or threat. Final impairment listings will be available with the next Integrated Report and are contingent on federal approval.

The concentrations of most metals in benthic sediment in the Smith River were typically within the background ranges provided by NOAA, except for arsenic and zinc, which regularly exceeded the background ranges (NOAA, 2008). For other metals like cadmium, chromium, copper, and iron, the concentrations generally increased from upstream to downstream and the highest concentrations were observed at the lower sites. The sediment samples from Sheep Creek and Calf Creek (reference stream) had greater concentrations of arsenic, chromium, copper, iron, and zinc than any of the Smith River samples. These trends likely reflect the weathering of geologic formations and local mineralized areas.

6.0 ACKNOWLEDGEMENTS

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¹ Several DEQ documents listed here were developed during the initial phases of the Smith River Algae Study and refer to "nuisance" algae. Throughout the Algae Study and Metals Study reports, this term has been superseded by "excess" or "undesirable" to ensure greater consistency with Montana water quality standards.

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APPENDIX A: LOAD CALCULATIONS FOR SMITH RIVER AND SHEEP CREEK

ORANGE CELLS = CALCULATED FROM J‐FLAG VALUE RED CELLS = NON‐DETECT, CALCULATED FROM 1/2 DETECT LIMIT

ORANGE CELLS = CALCULATED FROM J‐FLAG VALUE

RED CELLS = NON‐DETECT, CALCULATED FROM 1/2 DETECT LIMIT