

**Alaska Department of Environmental Conservation
555 Cordova Street
Anchorage, Alaska 99501**

**Total Maximum Daily Loads
for Antimony, Arsenic, and Iron in the
Waters of
Slate Creek in Denali National Park, Alaska**

April 2014 DRAFT

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ACRONYMS

°C	degrees Celsius
°F	degrees Fahrenheit
%	Percent
AAC	Alaska Administrative Code
APDES	Alaska Pollutant Discharge Elimination System
atm	Atmospheric Pressure
BMP	Best Management Practice
CaCO ₃	Calcium Carbonate
CCC	Criterion Continuous Concentration
CEC	Cation Exchange Capacity
CFR	Code of Federal Regulations
cfs	Cubic Feet per Second
cm	Centimeters
CMC	Criteria Maximum Concentration
CWA	Clean Water Act
DDL	Diffuse Double Layer
DEC	Department of Environmental Conservation
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EPA	Environmental Protection Agency
ft/s	Feet per Second
g/cm ³	Grams per Cubic Centimeter
HFO	Hydrous Ferric Oxide
in	Inches
kJ/mol	Kilo Joules per Mole
LA	Load Allocation
meq/100g	Milliequivalents per 100 Grams
µg/L	Micrograms per Liter
mg/kg	Milligrams per Kilogram
mg/L	Milligrams per Liter
mi ²	Square Miles
mm/s	Millimeters per Second
mol/L	Moles per Liter

MOS	Margin of Safety
NED	National Elevation Dataset
NLCD	National Land Cover Dataset
NPDES	National Pollutant Discharge Elimination System
NPS	National Park Service
ORP	Oxidation Reduction Potential
pE	Reduction Potential
PEL	Probable Effects Level
POM	Particulate Organic Matter
PHREEQC	pH-Redox-Equilibrium-Equations in C
SI	Saturation Index
SQuiRTs	Screening Quick Reference Tables
SSURGO	Soil Survey Geographic
TEL	Threshold Effects Level
TMDL	Total Maximum Daily Load
UAF	University Alaska at Fairbanks
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WLA	Wasteload Allocation
WRCC	Western Regional Climate Center

**Total Maximum Daily Loads (TMDLs) for
Antimony, Arsenic, and Iron in
Slate Creek, Alaska**

TMDL at a Glance:

<i>Water Quality Limited?</i>	Yes
<i>Alaska ID Number:</i>	40510-003
<i>Criteria of Concern:</i>	Antimony, Arsenic, and Iron
<i>Designated Uses Affected:</i>	(1) Water supply, (2) water recreation, and (3) growth and propagation of fish, shellfish, other aquatic life, and wildlife
<i>Major Source(s):</i>	Historic Mining
<i>Loading Capacity:</i>	6 µg/L Antimony; 10 µg/L Arsenic; 1,000 µg/L Iron
<i>Wasteload Allocation (WLA):</i>	6 µg/L Antimony; 10 µg/L Arsenic; 1,000 µg/L Iron
<i>Load Allocations (LA):</i>	6 µg/L Antimony; 10 µg/L Arsenic; 1,000 µg/L Iron
<i>Margin of Safety (MOS):</i>	Implicit
<i>Future Growth:</i>	None
<i>Necessary Reductions:</i>	96% Antimony, 86% Arsenic, 66% Iron

Total Antimony, Arsenic, Iron Measured as Water Concentrations (µg/L) ^a								
Waterbody	Pollutant	Loading Capacity	Future WLA	LA	MOS	Future Growth ^b	Maximum Observed ^c	Percent Reduction to Meet LA
Slate Creek	Antimony	6	6	6	Implicit	N/A	158	96%
	Arsenic	10	10	10	Implicit	N/A	69.9	86%
	Iron, dissolved	1,000	1,000	1,000	Implicit	N/A	2,980	66%

^a Applicable water quality criteria for antimony, arsenic, and iron apply year round in Slate Creek; presented as micrograms per liter (µg/L).

^b N/A = not applicable

^c Maximum observed after August 2010, which is after the most recent National Park Service restoration activities.

Executive Summary

Slate Creek is a 2.2 square mile watershed located in Denali National Park in interior Alaska. Alaska's Department of Environmental Conservation (DEC) first included Slate Creek on the Clean Water Act (CWA) section 303(d) list as impaired for turbidity in 1994. This original listing was associated with hard rock mining activities in the watershed, resulting in approximately four acres of disturbed area (USEPA 2013). Subsequent restoration activities improved sediment and turbidity conditions in the watershed. Monitoring indicated that the creek is now meeting the turbidity water quality standard (Brabets and Ourso 2013) and DEC has proposed to remove Slate Creek from the 2012 303(d) list for turbidity (ADEC 2012a). However, this same monitoring effort identified exceedances of the antimony, arsenic, and iron water quality standards. Therefore, the state of Alaska has included Slate Creek on its 2012 section 303(d) list as water quality limited due to antimony and arsenic and identified mining as the expected pollutant source (ADEC 2012a). Subsequent data analyses indicated that iron also is not meeting water quality standards. The presence of elevated levels of antimony, arsenic, and iron indicates the need for a Total Maximum Daily Load (TMDL) and additional restoration in the watershed.

A TMDL is established in this document to meet the requirements of Section 303(d)(1)(C) of the CWA and the U.S. Environmental Protection Agency's (EPA) implementing regulations (40 CFR Part 130), which require the establishment of a TMDL to achieve water quality standards when a waterbody is water quality-limited. A TMDL represents the amount of a pollutant the waterbody can assimilate while maintaining compliance with applicable water quality standards. A TMDL is composed of the sum of individual wasteload allocations (WLAs) for point sources and load allocations (LAs) for nonpoint sources and natural background loads. In addition, the TMDL must include a margin of safety (MOS), either implicitly or explicitly, that accounts for the uncertainty in the relationship between pollutant loads and the quality of the receiving waterbody and an allocation for future sources, if applicable.

This document establishes TMDLs to address the antimony, arsenic, and iron impairments in Slate Creek. The Slate Creek watershed is in the Kantishna Hills, approximately five miles west of Wonder Lake. The Kantishna Hills are lower mountains in the northern part of the Alaska Mountain Range.

Kantishna Hills is an area that was heavily mined throughout the last century, particularly for placer gold. Mining altered the natural system at Kantishna Hills, resulting in degraded water quality and riparian zones, mining waste, increased turbidity, and heavy metals contamination throughout the area (Environmental Compliance Consultants, Inc. et al. no date). Stream channels were also heavily modified and settling ponds were constructed (Brabets and Ourso 2013). Gold, silver, antimony, lead, and zinc were the primary mining products extracted from the Kantishna Hills area.

The Slate Creek watershed is a small portion of the larger Kantishna Hills area. In the Slate Creek watershed, mining was limited to hard rock mining (as opposed to the placer mining that is prevalent in other areas of the Kantishna Hills). This hard rock mining was for antimony from stibnite (Sb_2S_3) quartz veins. Arsenic and iron are present in the Slate Creek watershed due to pyrite (FeS_2) and arsenopyrite (FeAsS), which are commonly associated with stibnite.

Applicable water quality standards for arsenic, antimony, and iron in Slate Creek establish water quality criteria for the protection of designated uses for water supply, water recreation, and growth and propagation of fish, shellfish, other aquatic life, and wildlife. The TMDL numeric targets for antimony, arsenic, and iron in Slate Creek are expressed as concentrations, equivalent to Alaska's numeric water quality criteria of 6 $\mu\text{g/L}$ for antimony, 10 $\mu\text{g/L}$ for arsenic, and 1,000 $\mu\text{g/L}$ for iron. For both antimony and arsenic, the drinking water criterion is the lowest and, therefore, most protective of the water quality criteria. This criterion protects all designated uses, including the water supply designated use, and is based on the total recoverable concentration in ambient water. For iron, the chronic aquatic life criterion is the lowest and, therefore, most protective of the water

quality criteria. It is based on the dissolved (biologically active) fraction of metal concentrations in ambient water (18 AAC 70.020(b)(2)(A)(i)).

A concentration-based TMDL is appropriate for Slate Creek because using a more complicated analysis to estimate antimony, arsenic, and iron loads from former mine drainage would require additional data collection and would not provide additional guidance or benefit to the subsequent planning and implementation actions. The state water quality criteria directly address the basis for section 303(d)-listing and the only known source of impairments (antimony, arsenic, and iron) is drainage from the adjacent former antimony mine and related sources, such as internal loading. Therefore, the TMDLs for antimony, arsenic, and iron in Slate Creek are expressed as concentrations of 6 µg/L for antimony, 10 µg/L for arsenic, and 1,000 µg/L for iron. The only point source in the watershed is potential construction associated with restoration or park enhancement activities, which receive future WLAs. The WLAs (for the point source) and LAs (for the nonpoint sources) are set equal to the concentration-based TMDL numeric targets. These TMDLs included an implicit MOS and because future development is not expected, there is no reserve allocation for future growth. When compared to the existing concentrations, which are calculated using the maximum observed concentration after the most recent restoration efforts in 2010, necessary reductions ranged from 66 percent (%) to 96%.

Reducing concentrations of antimony, arsenic, and iron in Slate Creek may involve further efforts to control runoff from the former antimony mine while considering the contribution of internal loadings from creek-bottom sediment. Various restoration efforts have taken place at Slate Creek since 1997, when the National Park Service (NPS) developed a recovery plan. These efforts include: upland restoration to improve drainage from the exposed mine site, tailings removal, modification of groundwater flows, and draining and filling an old settling pond (Brabets and Ourso 2013). During the 1997-1998 restoration, tailings were used to reconstruct the floodplain and create an anoxic drain with geotextiles and limestone to filter groundwater and buffer the acid mine drainage from the pit mine (USEPA 2013). In 2010, an extended tailings pile was excavated. The tailings were saturated from hillside seeps and precipitation and were comprised of fine silt, clay and gravel. Because of this excavation, a large volume of unstable substrate was removed from the floodplain, thus eliminating materials that were contributing to accelerated erosion and sedimentation and turbidity (Brabets and Ourso 2013). Erosion blankets were installed along the newly contoured valley side slopes to prevent additional erosion. In addition to removing highly erosive materials, the channel was rerouted to avoid the main pit from the former mine (Brabets and Ourso 2013).

Implementation of the Slate Creek TMDL should focus on increased reductions from former mining runoff and management of the creek-bottom iron sediment load. The most effective means of addressing the historic mining source is preventing contaminated runoff from entering Slate Creek and managing the iron concentrations in water and sediment. Healthy riparian areas will ensure runoff is filtered prior to it reaching Slate Creek. Implementation of the TMDL will occur through efforts by the NPS and their partners to remediate the former antimony mine (see Section 7).

Follow-up monitoring is recommended to track the progress of TMDL implementation and subsequent water quality response, track best management practice effectiveness, and track the water quality of Slate Creek to evaluate progress towards meeting water quality standards.

1. Overview

Section 303(d)(1)(C) of the Clean Water Act (CWA) and the U.S. Environmental Protection Agency's (EPA) implementing regulations (40 CFR Part 130 [note: CFR is the Code of Federal Regulations]) require the establishment of a Total Maximum Daily Load (TMDL) to achieve state water quality standards when a waterbody is water quality-limited. A TMDL identifies the amount of a pollutant that a waterbody can assimilate and still maintain compliance with applicable water quality standards. TMDLs identify the level of pollutant control needed to reduce pollutant inputs to a level (or "load") that fully supports the designated uses of a given waterbody and include an appropriate margin of safety to account for uncertainty or lack of knowledge regarding the pollutant loads and the response of the receiving water. The mechanisms used to address water quality problems after the TMDL is developed can include a combination of best management practices (BMPs) for nonpoint sources and/or effluent limits and monitoring required through EPA's National Pollutant Discharge Elimination System (NPDES) permits (or in Alaska, the Alaska Pollutant Discharge Elimination System [APDES] permits) for point sources.

Alaska's Department of Environmental Conservation (DEC) first included Slate Creek on the section 303(d) list as impaired for turbidity in 1994. This original listing was associated with hard rock mining activities in the watershed, resulting in approximately four acres of disturbed area (USEPA 2013). Specifically, erosion of unstable areas increased the turbidity above the water quality criteria. The National Park Service (NPS) and other partners performed restoration activities on the creek in 1997-1998 and 2010, including the removal of mining debris and tailings in the floodplain as well as restructuring of the stream (USEPA 2013). Subsequent monitoring by the United States Geological Survey (USGS) in 2008-2011 indicated that the creek is now meeting the turbidity water quality criteria (Brabets and Ourso 2013) and DEC has proposed to remove Slate Creek from the 2012 303(d) list for turbidity (ADEC 2012a).

However, the USGS sampling effort did identify exceedances of the antimony, arsenic, and iron water quality criteria (Brabets and Ourso 2013). The waterbody is included as impaired for arsenic and antimony on the Alaska 2012 section 303(d) list (ADEC 2012a; note: pending EPA approval as of March 2014). Table 1-1 summarizes the information included in the Alaska 2012 section 303(d) list for Slate Creek. Subsequent data analyses show that iron is also exceeding the water quality criterion (see Section 3.2); therefore, iron is also included in this TMDL report. The major source of antimony, arsenic, and iron to Slate Creek is historic mining. Other potential sources, some of which are related to the historic mining, include natural sources and internal cycling from deposited sediment. This document describes the overall watershed setting as well as water quality standards, the technical approach, and TMDLs and allocations associated with the Slate Creek arsenic, antimony, and iron impairments and provides restoration and monitoring recommendations.

Table 1-1. Slate Creek section 303(d) listing information from DEC's 2012 Integrated Report

Alaska ID Number	Waterbody	Area of Concern	Water Quality Standard	Pollutant Parameters	Pollutant Sources
40510-003	Slate Creek	2.5 miles	Toxic & Other Deleterious Organic and Inorganic Substances	Metals – Antimony, Arsenic	Mining
<p>Slate Creek was placed on the 1994 Section 303(d) list for non-attainment of the turbidity water quality standard because of historic placer mining activities. Current National Park Service (NPS) policy will not permit mining. A recovery plan implementation began in August 1997 and continued through 2002. The recovery plan included restoration objectives for 4 acres of disturbed upland and stream channel areas in the vicinity of the old antimony mine site. Objectives included placement of fill over exposed antimony ore body, reconfiguration of the stream channel, increases in the pH of acidic soils, and revegetation of disturbed soils with willow and alder seedlings. Slate Creek was visited by DEC staff and NPS staff in 2006 for a general site review of the recovery plan implementation that was completed in 2002. The 2006 site visit revealed that the recovery plan was not successful and that in many areas actions implemented were no longer performing their functions properly. NPS staff visited Slate Creek twice in the 2007 field season to gather information to develop an amended recovery concept plan. The amended plans have been developed to address the surface and groundwater drainage for erosion control and acidic mitigation. If funding becomes available, work will begin in 2010. NPS and DEC staff conducted a site visit in 2011. In several areas the restoration is failing and much of the vegetation failed to establish. Water quality monitoring by USGS from 2008-2011 indicate that the creek is meeting the turbidity standard, however there are exceedances of antimony and arsenic standards.</p>					

Source: ADEC (2012a); pending EPA approval as of March 2014.

1.1. Location and Setting

The Slate Creek watershed is in the Kantishna Hills section of Denali National Park and Preserve in interior Alaska, approximately five miles west of Wonder Lake (Figure 1-1). The Kantishna Hills are lower mountains in the northern part of the Alaska Mountain Range. Kantishna Hills is an area that was heavily mined throughout the last century, particularly for placer gold. Mining altered the natural system at Kantishna Hills, causing removal of natural topsoil and leaving exposed mineral-laden substrate, thereby resulting in degraded water quality and riparian zones, mining waste, increased turbidity and heavy metals contamination throughout the area (Brabets and Ourso 2013). Stream channels were also heavily modified and settling ponds were constructed (Brabets and Ourso 2013). Gold, silver, antimony, lead, and zinc were the primary mining products extracted from the larger Kantishna Hills area.

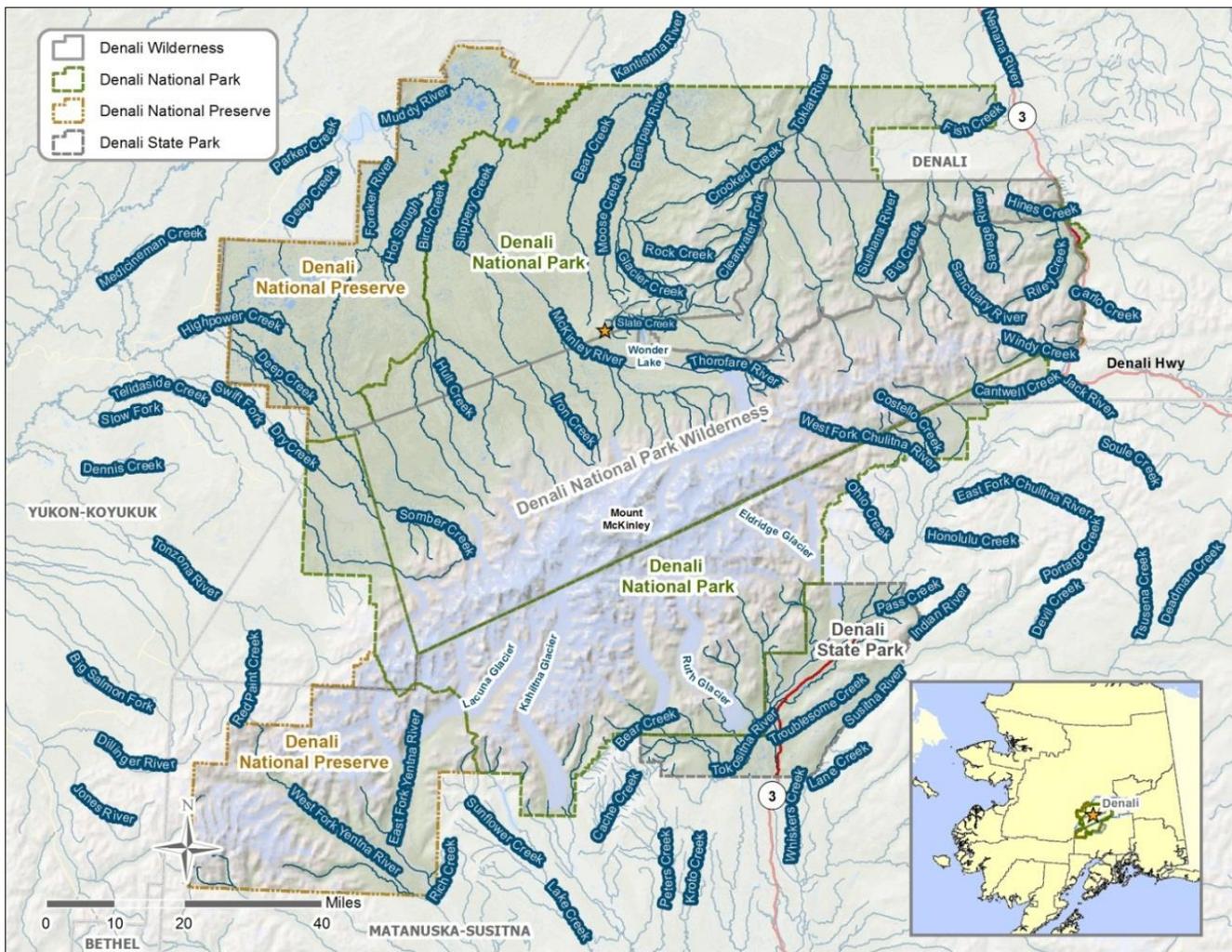


Figure 1-1. Regional location of the Slate Creek study area.

Slate Creek is an approximately two-mile-long tributary to Eldorado Creek and the larger Moose Creek in the Kantishna River watershed (Figure 1-1). The Slate Creek drainage area is 2.2 square miles (mi^2) and elevation ranges from approximately 650 to 1,150 feet (Figure 1-2 and Figure 1-3). The headwaters of Slate Creek flow through a former antimony mine. Specifically, Slate Creek watershed mining was limited to hard rock mining (as opposed to the placer mining that is prevalent in other areas of the Kantishna Hills). This hard rock mining was for antimony from stibnite (Sb_2S_3) quartz veins. Arsenic and iron are present in the Slate Creek watershed due to pyrite (FeS_2) and arsenopyrite (FeAsS), which are commonly associated with stibnite. Mining near Slate Creek

ended by 1985 with the Kantishna Mining District-wide mining injunction (USEPA 2013). Slate Creek was placed on Alaska's 2012 section 303(d) list for antimony and arsenic impairments (ADEC 2012a) and iron exceedances have also been observed (Section 3.2).

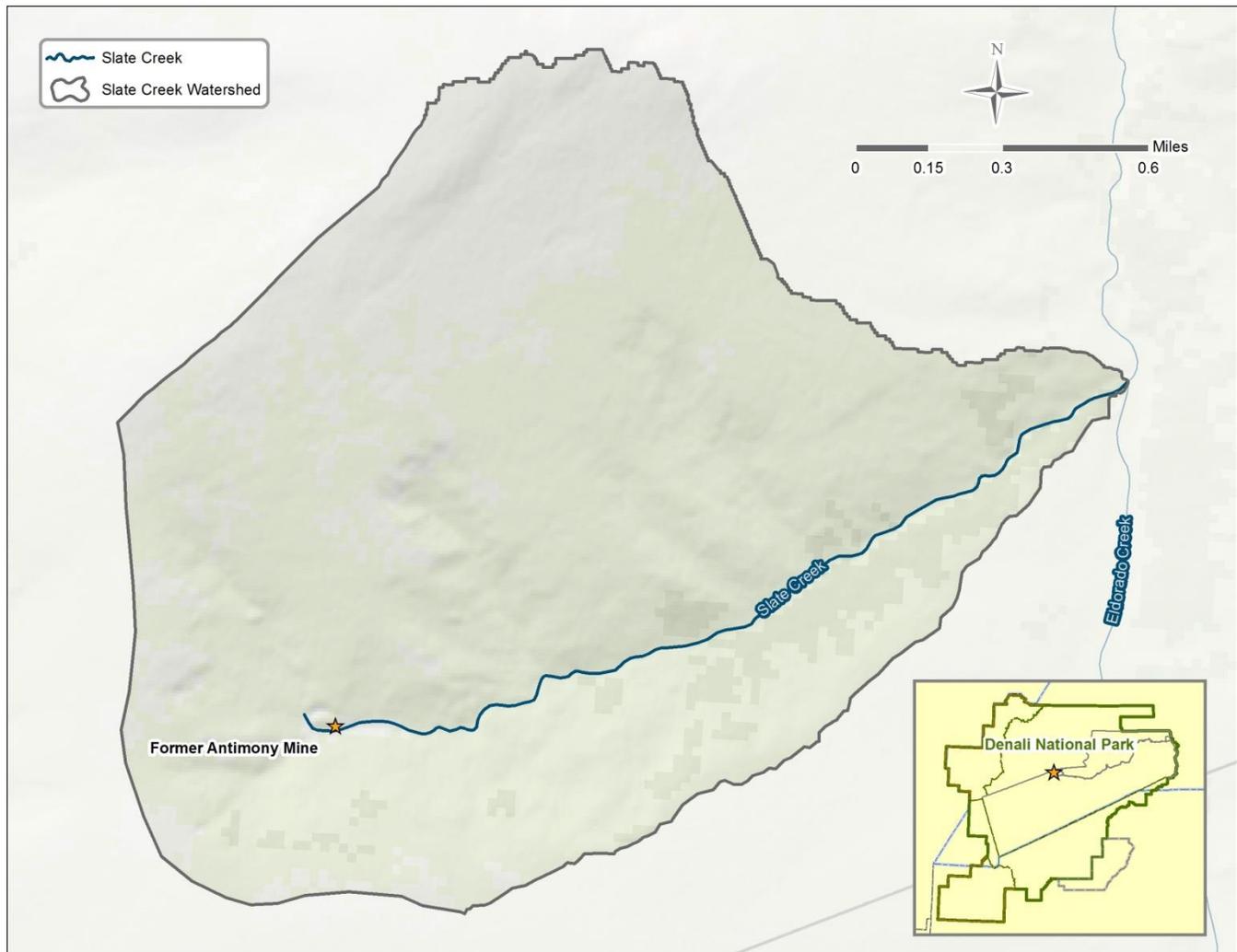


Figure 1-2. Slate Creek watershed study area.

1.2. Population

Slate Creek lies in an unpopulated portion of the Denali National Park. There is no road access to the creek currently. The only anthropogenic activity in the watershed was from the historic antimony mine.

1.3. Topography

Elevation data were obtained from the USGS National Elevation Dataset (NED). The elevation of the Slate Creek watershed ranges from 650 feet near the mouth at Eldorado Creek to 1,150 feet near the headwaters at Brooker Mountain (Figure 1-3). Elevation at the old antimony mine is near 820 feet (USGS 2013).

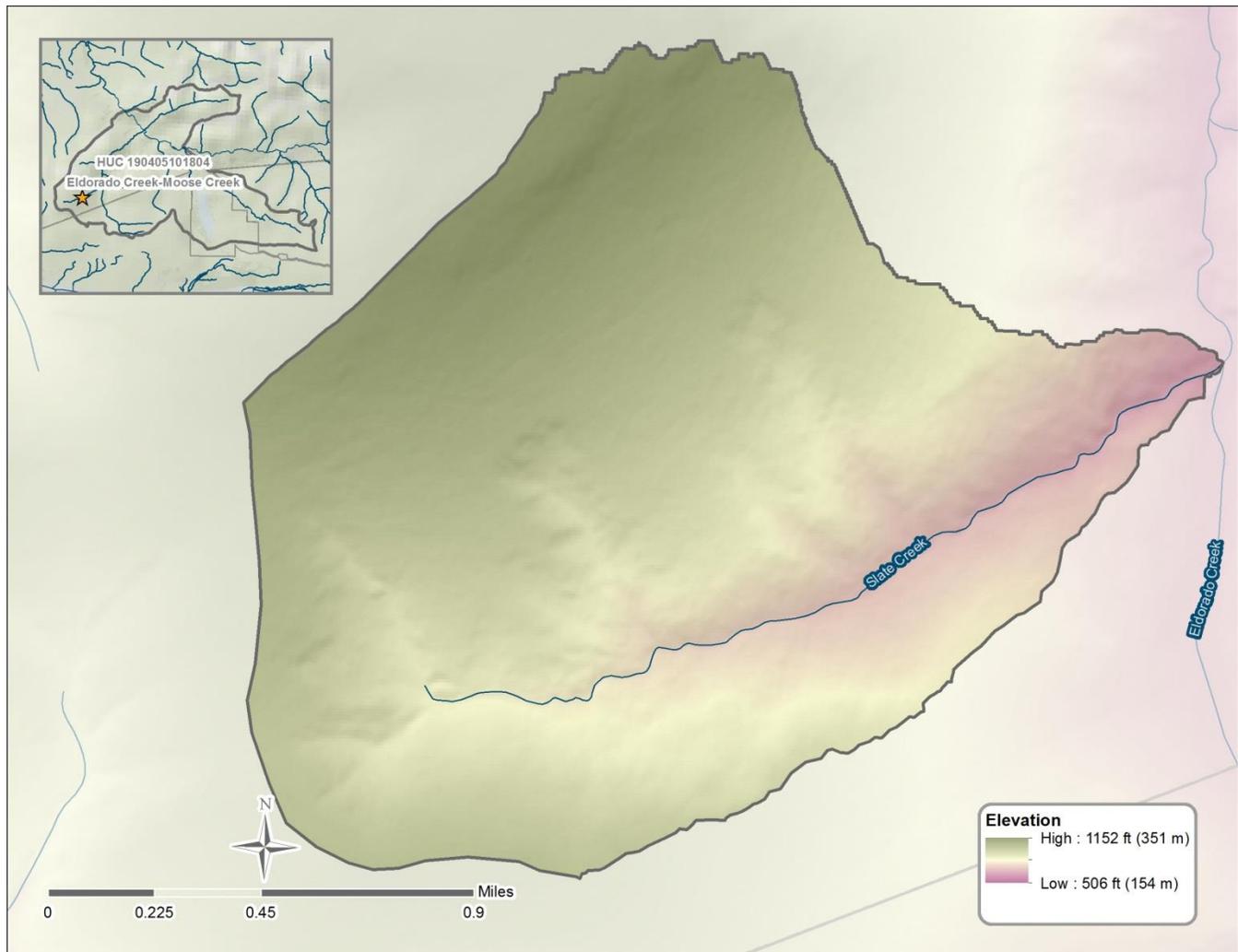


Figure 1-3. Elevation in the Slate Creek watershed (Source: NED).

1.4. Land Use

Land use data were obtained from the 2001 USGS National Land Cover Data set (NLCD; Homer et al. 2007). The NLCD data are based on satellite imagery from 2001. Land in the Slate Creek watershed is predominantly shrub/scrub (70 percent [%]) and less than 7% of the watershed is forested (Figure 1-4 and Table 1-2). Various areas of the Slate Creek drainage are classified as palustrine scrub-shrub wetlands with broad-leaved deciduous vegetation, needle-leaved evergreens and emergent wetlands with persistent vegetation (Homer et al. 2007; USFWS 2013). A former antimony mine is located at the headwaters of the creek. The soils are saturated to the surface in some areas; however, due to past mining activities the stream channels have very little vegetation (Brabets and Ourso 2013).

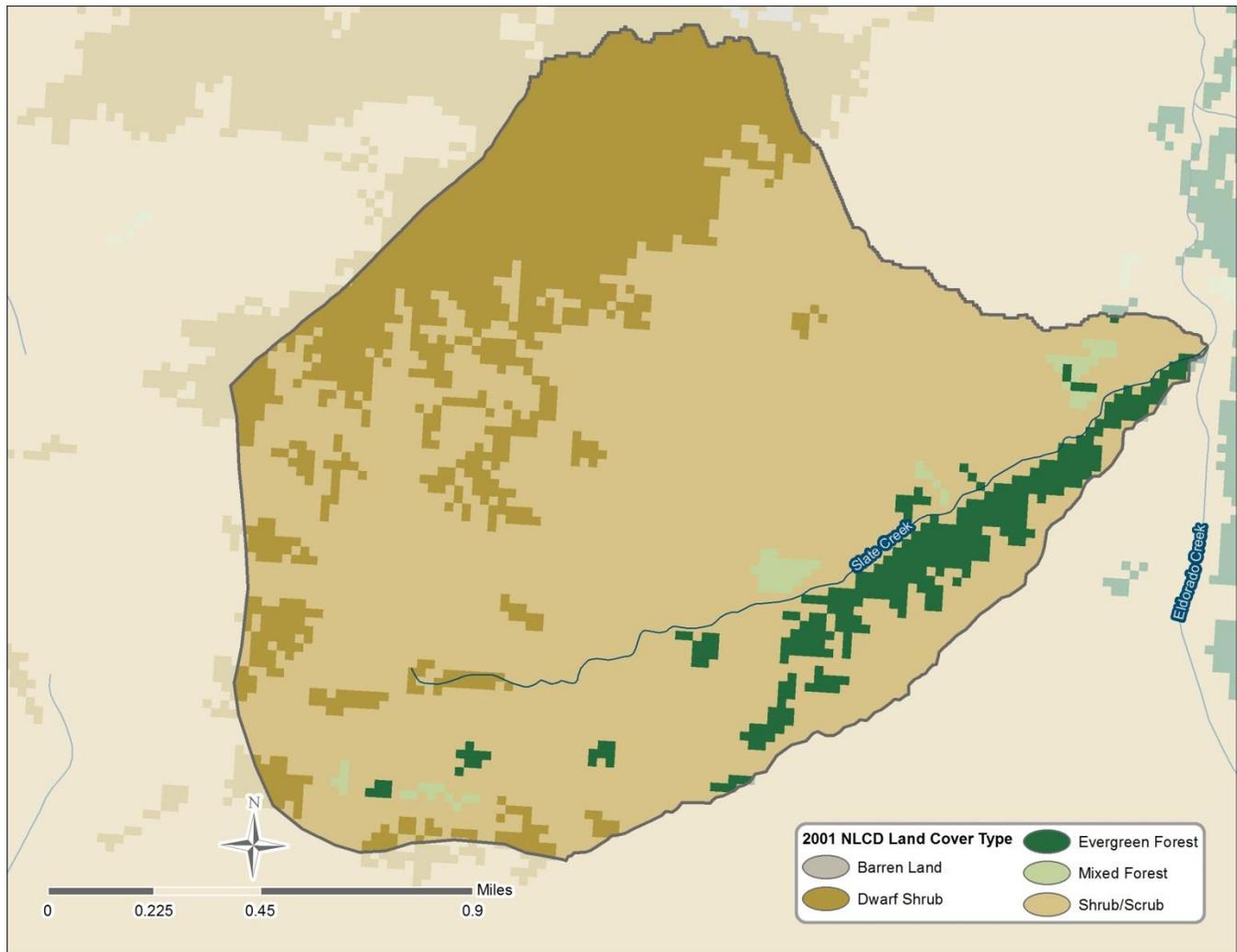


Figure 1-4. Land use in the Slate Creek watershed (Source: NLCD 2001).

Table 1-2. Land use/cover distribution in the Slate Creek watershed

Land Use	Area (acres)	Percent of total area
Evergreen Forest	73	5.1 %
Mixed Forest	15	1.1 %
Dwarf Shrub	334	23.6 %
Shrub/Scrub	997	70.3 %
TOTAL	1,419	100.0 %

1.5. Soils and Geology

According to the USGS Mineral Resources On-Line Spatial Data the entire Slate Creek watershed is part of the pelitic and quartzose schist of the Alaska Range (USGS 2014). The antimony deposit in the Slate Creek watershed is a quartzite unit of the Birch Creek Schist (Brabets and Ourso 2013). The majority of the soils in the Slate Creek watershed belong to Hydrologic Soil Group D, while the rest are Hydrologic Soil Group B (NRCS 2009). D soils have high runoff potential and very low infiltration rates with a clay layer at or near the surface. B soils typically have moderate infiltration rates with moderately well to well-drained soils. Figure 1-5 and Table 1-3 summarize the Slate Creek watershed soil information.

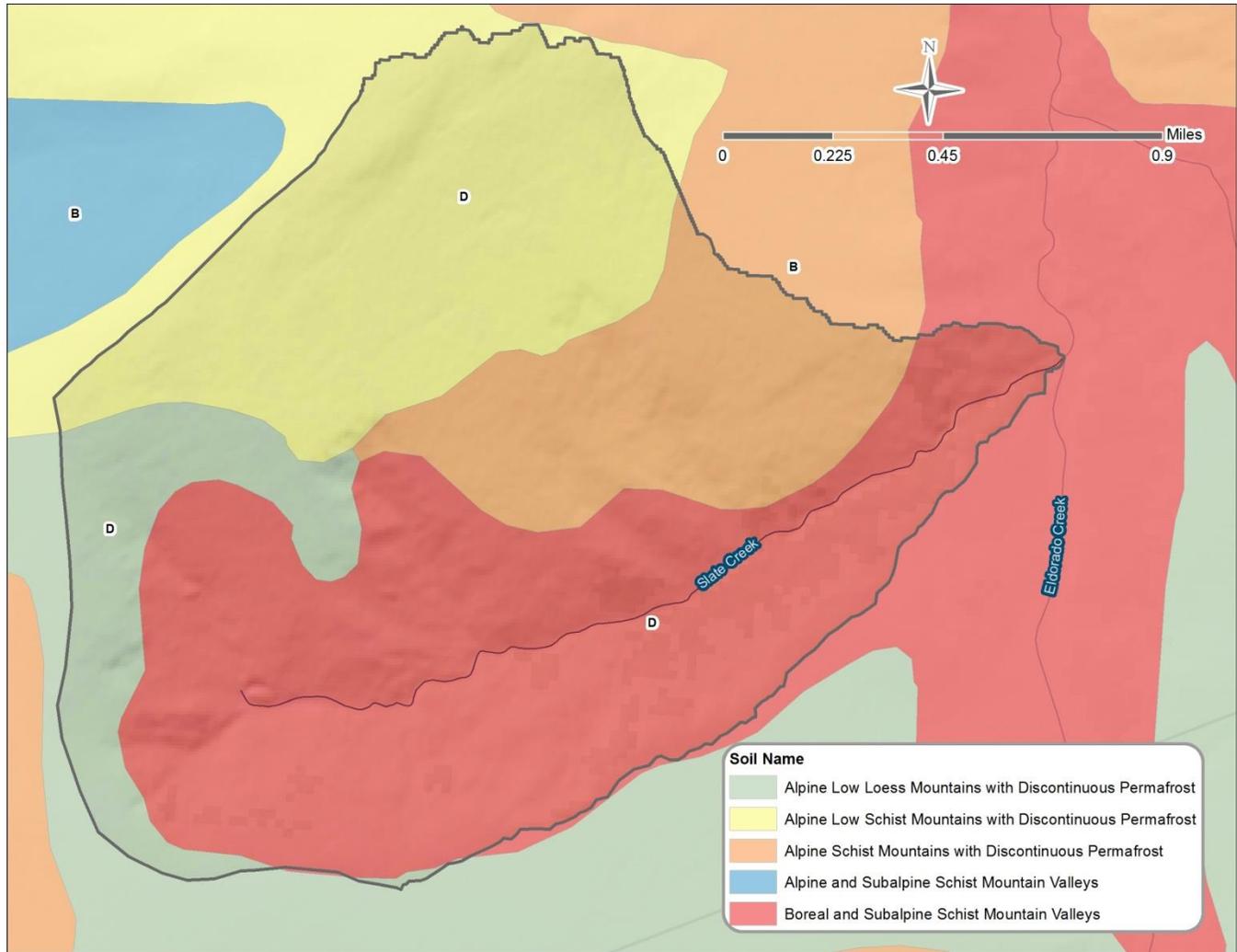


Figure 1-5. Soil classification in the Slate Creek watershed (Source: SSURGO).

Table 1-3. Soil distribution in the Slate Creek watershed

Soil Name	Area (Acres)	Percent Area	Hydrologic Soil Group	Percent Clay - Dominant Condition	Drainage Class - Dominant Condition	Drainage Class - Wettest
Alpine Schist Mountains with Discontinuous Permafrost	234	16%	B	15	Well drained	Very poorly drained
Alpine Low Loess Mountains with Discontinuous Permafrost	144	10%	D	5	Poorly drained	Very poorly drained
Alpine Low Schist Mountains with Discontinuous Permafrost	387	27%	D	13.9	Poorly drained	Very poorly drained
Boreal and Subalpine Schist Mountain Valleys	656	46%	D	14	Poorly drained	Poorly drained

1.6. Climate

The Slate Creek watershed is located in the “interior” climate zone of Alaska, between the transitional and arctic zones. Temperatures extremes in the interior zone near Denali National Park and Preserve can range from a high of over 90 degrees Fahrenheit (°F) in the summer to below -50 °F in the winter (Western Regional Climate Center [WRCC] 2014). Climate is typically cold with dry winters and warm but short summers. Average annual precipitation was 15.12 inches for the period of record (1949-2012) at the McKinley Park Station, located over 60 miles east-northeast of the Slate Creek watershed and at 1,000 feet in elevation higher than Slate Creek. The average monthly precipitation for the period of record ranges from 0.37 inches in April to 3.14 inches in July. The highest temperatures occur in July on average with a monthly average temperature of about 55°F. The lowest air temperatures occur in January with an average monthly temperature of about 0°F (Figure 1-6 and Table 1-4).

Autumn begins in early September and ends in mid-October with temperatures falling in September and snowfalls increasing in October. Winter lasts from mid-October to early April, with the coldest temperatures typically occurring in January. Spring begins in late April and May with less precipitation and increasing temperatures. Figure 1-6 and Table 1-4 present a summary of monthly averages for rainfall, snowfall and temperature at the McKinley Park Station, based on the period of record at the station from September 1949 to September 2012.

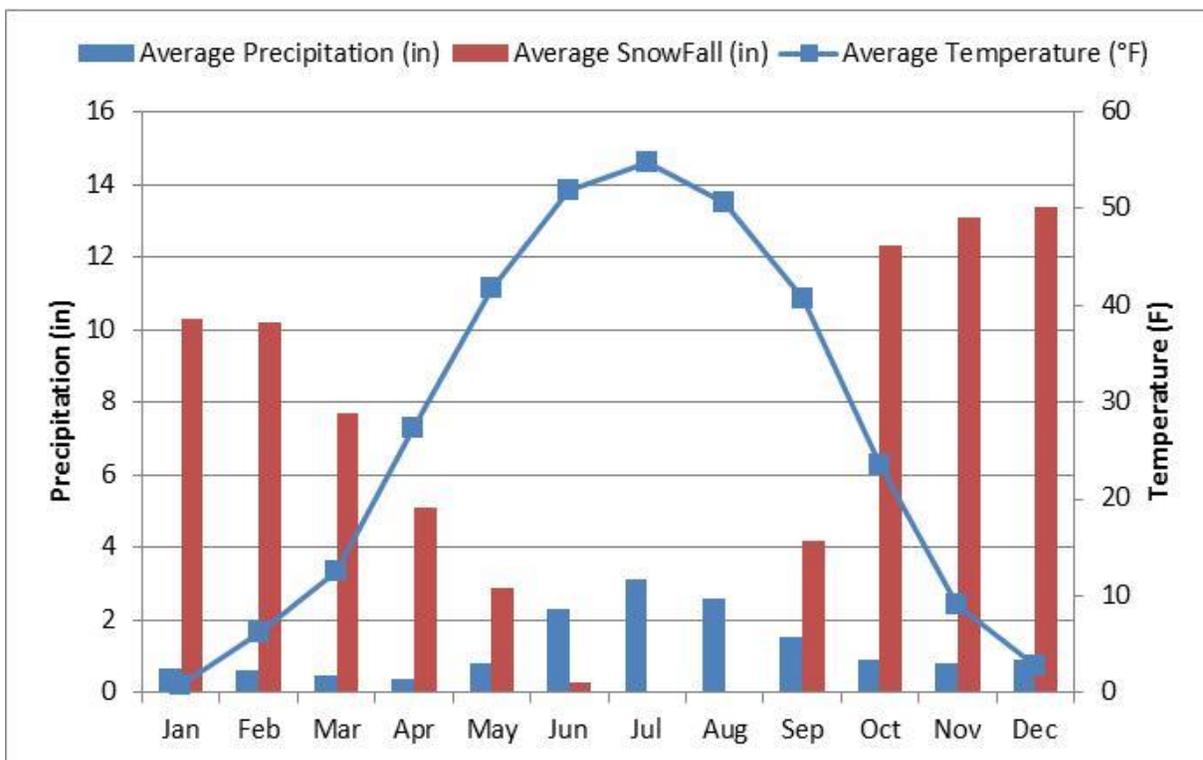


Figure 1-6. Monthly average precipitation and temperatures at McKinley Park.

Table 1-4. Monthly average precipitation, snowfall, and temperatures at McKinley Park

Measurement (units)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Average Precipitation (in)	0.68	0.6	0.46	0.37	0.8	2.32	3.14	2.57	1.54	0.92	0.83	0.9
Average Snowfall (in)	10.3	10.2	7.7	5.1	2.9	0.3	0	0	4.2	12.3	13.1	13.4
Average Temperature (°F)	0.7	6.1	12.6	27.3	41.75	51.95	54.85	50.65	40.65	23.45	9.1	2.8

1.7. Hydrology and Waterbody Characteristics

Slate Creek flows east-northeast from the southwest end of Brooker Mountain to Eldorado Creek in the Kantishna River watershed. The creek drains an area of approximately 2.2 mi². Slate Creek is considered a calcium bicarbonate water (Brabets and Ourso 2013). The stream banks contain non-vegetated tailing piles of gravels, cobbles and boulders (Brabets and Ourso 2013). The creek is severely embedded and exhibits the characteristic rust-colored streambeds indicative of high iron levels (Brabets and Ourso 2013). Most of the annual flow in Slate Creek is from mid-May to mid-October. Snowmelt occurs in late May and early June, resulting in higher than average flows, while low flows occur in October as air temperature cools and rainfall decreases. During the USGS 2008-2011 investigation, stream flow on Slate Creek at the mine site ranged from 0.3 to 2.1 cubic feet per second (cfs) (Brabets and Ourso 2013). Based on a comparison with an unmined reference stream (Rock Creek), the runoff characteristics on a unit stream flow per area basis at Slate Creek were similar to Rock Creek (Brabets and Ourso 2013).

1.8. Previous Restoration Efforts

Various restoration efforts have taken place at Slate Creek since 1997, when the NPS developed a recovery plan, including upland restoration to improve drainage from the exposed mine site, tailings removal, modification of groundwater flows, and draining and filling an old settling pond (Brabets and Ourso 2013). During the 1997-1998 restoration, tailings were used to reconstruct the floodplain and create an anoxic drain with geotextiles and limestone to filter groundwater and buffer the acid mine drainage from the pit mine (USEPA 2013). In 2010, an extended tailings pile was excavated. The tailings were saturated from hillside seeps and precipitation and were comprised of clay, silt, and gravel. Because of this excavation, a large volume of unstable substrate was removed from the floodplain, thus eliminating materials that were contributing to accelerated erosion and sedimentation and turbidity (Brabets and Ourso 2013). Erosion blankets were installed along the newly contoured valley side slopes to prevent additional erosion. In addition to removing highly erosive materials, the channel was rerouted to avoid the main pit from the former mine (Brabets and Ourso 2013). These activities have improved erosion and the associated turbidity conditions in the watershed; however, due to effects from the historic mining such as the continued presence of mine tailings, water quality measurements of antimony, arsenic, and iron remain elevated. Figure 1-7 shows the new Slate Creek stream channel during construction (left) and shortly after construction (right) in 2010.



Figure 1-7. Slate Creek stream channel reconstruction (during construction: left, post construction: right [USEPA 2013]).

2. Water Quality Standards and TMDL Target

Water quality standards designate the “uses” to be protected (e.g., water supply, recreation, aquatic life) and the “criteria” for their protection (e.g., how much of a pollutant can be present in a waterbody without impairing its designated uses). TMDLs are developed to meet applicable water quality standards, which may be expressed as numeric water quality criteria or narrative criteria for the support of designated uses. The TMDL target identifies the numeric goals or endpoints for the TMDL that equate to attainment of the water quality standards. The TMDL target may be equivalent to a numeric water quality criterion where one exists, or it may represent a quantitative interpretation of a narrative criterion. This section reviews the applicable water quality standards and identifies appropriate TMDL targets for calculation of the antimony, arsenic, and iron TMDLs for Slate Creek.

2.1. Applicable Water Quality Standards

Title 18, Chapter 70 of the Alaska Administrative Code (AAC) establishes water quality standards for the waters of Alaska (ADEC 2012b), including both the designated uses to be protected and the water quality criteria necessary to protect the uses, as described below. State water quality criteria are defined for both marine and fresh waterbodies. The fresh water criteria are applicable to Slate Creek.

2.1.1. Designated Uses

Designated uses for Alaska’s waters are established by regulation and are specified in the State of Alaska Water Quality Standards (18 AAC 70). For fresh waters of the state, these designated uses include (1) water supply, (2) water recreation, and (3) growth and propagation of fish, shellfish, other aquatic life, and wildlife. All designated uses must be addressed unless specifically exempted in Alaska. Therefore, the TMDL must use the most stringent of the criteria among all of the uses.

2.1.2. Water Quality Criteria

Slate Creek does not fully support its designated uses because of antimony, arsenic, and iron in the water column (Section 3.2.1). Water quality criteria for all designated uses are applicable to Slate Creek. Table 2-1 lists the water quality criteria for toxic and other deleterious organic and inorganic substances, on which the 303(d) listing for Slate Creek is based.

Table 2-1. Alaska water quality criteria for toxic and other deleterious organic and inorganic substances in fresh waters (18 AAC 70.020)

Designated Use	Description of Criteria
(11) Toxic and Other Deleterious Organic and Inorganic Substances	
(A) Water Supply	
(i) drinking, culinary, and food processing	The concentration of substances in water may not exceed the numeric criteria for drinking water and human health for consumption of water and aquatic organisms shown in the Alaska Water Quality Criteria Manual (see note 5). Substances may not be introduced at concentrations that cause, or can reasonably be expected to cause, either singly or in combination, odor, taste, or other adverse effects on the use.
(ii) agriculture, including irrigation and stock watering	The concentration of substances in water may not exceed the numeric criteria for drinking and stockwater and irrigation water shown in the Alaska Water Quality Criteria Manual (see note 5). Substances may not be introduced at concentrations that cause, or can reasonably be expected to cause, either singly or in combination, odor, taste, or other adverse effects on the use.
(iii) aquaculture	Same as (11)(C).
(iv) industrial	Concentrations of substances that pose hazards to worker contact may not be present.

Designated Use	Description of Criteria
(B) Water Recreation	
(i) contact recreation	The concentration of substances in water may not exceed the numeric criteria for drinking water shown in the Alaska Water Quality Criteria Manual (see note 5). Substances may not be introduced at concentrations that cause, or can reasonably be expected to cause, either singly or in combination, odor, taste, or other adverse effects on the use.
(ii) secondary recreation	Concentrations of substances that pose hazards to incidental human contact may not be present.
(C) Growth and Propagation of Fish, Shellfish, Other Aquatic Life, and Wildlife	The concentration of substances in water may not exceed the numeric criteria for aquatic life for fresh water and human health for consumption of aquatic organisms only shown in the Alaska Water Quality Criteria Manual (see note 5), or any chronic and acute criteria established in this chapter, for a toxic pollutant of concern to protect sensitive and biologically important life stages of resident species of this state. There may be no concentrations of toxic substances in water or in shoreline or bottom sediments, that, singly or in combination, cause, or reasonably can be expected to cause, adverse effects on aquatic life or produce undesirable or nuisance aquatic life, except as authorized by this chapter. Substances may not be present in concentrations that individually or in combination impart undesirable odor or taste to fish or other aquatic organisms, as determined by either bioassay or organoleptic tests.

Source: 18 AAC 70.020 (ADEC 2012b)

Note 5: Wherever cited in this subsection, the Alaska Water Quality Criteria Manual means the Alaska Water Quality Criteria for Toxic and Other Deleterious Organic and Inorganic Substances, dated December 12, 2008, adopted by reference in this subsection.

The State of Alaska has adopted EPA's water quality criteria for priority and non-priority pollutants in *Alaska Water Quality Criteria for Toxic and Other Deleterious Organic and Inorganic Substances* (ADEC 2008). Fresh water criteria relevant to Slate Creek are developed to protect various types of supply water, aquatic life, and human health, as described below (ADEC 2008).

- **Drinking water, stock water, and irrigation water:** Drinking water criteria are associated with fresh water uses for drinking, culinary, and food processing, and for contact recreation. Stock water and irrigation water are for fresh water use of water supply for agriculture.
- **Aquatic life:** Protection of aquatic life is associated with fresh water uses of aquaculture and growth and propagation of fish, shellfish, other aquatic life, and wildlife. These uses consist of two classifications: Criteria Maximum Concentration (CMC) and Criterion Continuous Concentration (CCC). The CMC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect, representing an acute criterion. The CCC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect, representing a chronic criterion.
- **Human health:** Water quality standards for fresh water uses of drinking, culinary, and food processing, and growth and propagation of fish, shellfish, other aquatic life, and wildlife. Criteria are based on the consumption of aquatic organisms only and both water and aquatic organisms.

Table 2-2 presents the applicable criteria for metals of concern in Slate Creek (ADEC 2008) (see Section 3.2.1 for a summary of the impairment analyses). For both antimony and arsenic, the drinking water criterion is the lowest and, therefore, most protective of the water quality criteria. This criterion protects all designated uses, including the water supply designated use, and is based on the total recoverable concentration in ambient water. For iron, the chronic aquatic life criterion is the lowest and, therefore, most protective of water quality criterion. It is based on the dissolved (biologically active) fraction of metal concentrations in ambient water.

Table 2-2. Freshwater water quality criteria for metals of concern in Slate Creek

Metal	Use	Criterion Value (micrograms per liter [µg/L])
Antimony	Drinking Water ¹	6
	Human Health for Consumption of Water & Aquatic Organisms	14
	Human Health for Consumption of Aquatic Organisms Only	4,300
Arsenic	Drinking Water ^{1,2}	10
	Stock Water ³	50
	Irrigation Water ⁴	100
	Acute Aquatic Life (CMC) – (1-hour average) ⁵ (dissolved) ^{7,8,9}	340
	Chronic Aquatic Life (CCC) – (4-hour average) ⁶ (dissolved) ^{8,9,10}	150
Iron (dissolved)	Irrigation Water ⁴	5,000
	Chronic Aquatic Life (CCC)	1,000

Source: ADEC (2008)

¹ Criteria in this table were obtained from ADEC, Alaska Drinking Water Regulations, as amended through November 9th, 2006 in 18 AAC 80.300(b). The drinking water primary maximum contaminant levels are used as water quality criteria to protect the drinking water and contact recreation uses. The criteria for metals will be measured using the total method that is consistent with drinking water regulations measurement protocol.

² With compliance to be reported as required under 18 AAC 80.305(b)(4).

³ Criteria were obtained from the Report of the Committee on Water Quality Criteria, (also known as the Green Book), 1968, Federal Water Pollution Control Administration, p. 135, Table IV-11.

⁴ Criteria were obtained from Water Quality Criteria, (also known as the Blue Book), 1972, National Academy of Sciences, National Academy of Engineering, Washington, D.C., p. 339, Table V-13.

⁵ Acute criteria are based on the average concentration of chemical pollutants during a one-hour period. One hour was chosen because it is a substantially shorter period than the length of most acute toxicity tests. Acute and chronic criteria are used together to develop water quality-based effluent limits.

⁶ Chronic criteria are based on the average concentration of chemical pollutants during a four-day period. A four-day averaging period was chosen because it is substantially shorter than most chronic toxicity tests. Chronic criteria are typically stricter than the acute criteria and are therefore used to protect ambient waters.

⁷ To calculate the dissolved criterion, the total recoverable criterion was multiplied by the conversion factor (339.8)(1.0) = 339.8 ~ 340

⁸ This recommended water quality criterion was derived from data for arsenic (III), but is applied here to total arsenic, which might imply that arsenic (III) and arsenic (V) are equally toxic to aquatic life and that their toxicities are additive. In the arsenic criteria document (EPA 440-5-84-033, January 1985), Species Mean Acute Values are given for both arsenic (III) and arsenic (V) for five species and the ratios of the SMAVs for each species range from 0.6 to 1.7. Chronic values are available for both arsenic (III) and arsenic (V) for one species; for the fathead minnow, the chronic value for arsenic (V) is 0.29 times the chronic value for arsenic (III). No data are known to be available concerning whether the toxicities of the forms of arsenic to aquatic organisms are additive.

⁹ This recommended criterion is based on a 304(a) aquatic life criterion that was issued in the 1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water, (EPA-820-B-96-001, September 1996). This value was derived using the GLI Guidelines (60FR15393-15399, March 23, 1995; 40CFR132 Appendix A); the difference between the 1985 Guidelines and the GLI Guidelines are explained on page iv of the 1995 Updates. None of the decisions concerning the derivation of this criterion were affected by any considerations that are specific to the Great Lakes.

¹⁰ To calculate the dissolved criterion, the total recoverable criterion was multiplied by the conversion factor (147.9)(1.0) = 147.9 ~ 150.

2.2. Sediment Quality Guidelines

Slate Creek is currently listed as impaired (upon approval of the 2012 303(d) list [ADEC 2012a]) due to elevated concentrations of metals impacting surface water. High metal concentrations in surface water can also be indicative of sediment impairment and monitoring studies have indicated high concentrations of arsenic, antimony, and iron in creek bottom sediments (Brabets and Ourso 2013; Ritchie et al. 2013). The relationship between sediment and water quality was evaluated through the use of an internal cycling model (see Section 4 below). To date, DEC has not adopted numeric sediment quality criteria for the evaluation of impacts to aquatic life. However, the DEC Contaminated Sites Remediation Program has issued the technical memorandum *Sediment Quality Guidelines* (ADEC 2013), which recommends using the Threshold Effects Levels (TELs) and Probable Effects Levels (PELs) for evaluating sediment quality (presented as milligrams per kilogram [mg/kg]). TELs define chemical sediment concentrations below which toxic effects are rarely observed in sensitive species, while PELs define concentrations above which effects are frequently or always observed.

Antimony and iron, however, do not have defined TELs or PELs. Antimony does have a “background” value, which is a concentration representative of non-anthropogenically impacted areas (note: this value is expected to reflect natural soils in the U.S. and is not an Alaska-specific value) and is not associated with adverse biological effects (Buchman 2008). The antimony “background” concentration, as provided in the *NOAA Screening Quick Reference Tables* (SQiRTs), is presented in Table 2-3 (Buchman 2008). Iron has a “background” value, which is a percentage representing the proportion of iron in non-anthropogenically impacted soils that is not associated with adverse biological effects. Arsenic has a “background” value in addition to the recommended freshwater TELs and PELs and all three values are shown in Table 2-3. The screening levels for antimony, arsenic, and iron were used to evaluate sediment quality data for Slate Creek (Sections 3.2 and 4).

Table 2-3. Freshwater sediment screening levels for metals of concern

Metal	Background (mg/kg)	TEL (mg/kg)	PEL (mg/kg)
Antimony	0.16	n/a	n/a
Arsenic	1.1	5.9	17
Iron (%)	0.99-1.8%	n/a	n/a

Source: Buchman (2008)

n/a = not applicable

2.3. Antidegradation

Alaska’s Water Quality Standards (18 AAC 70.015) also include an antidegradation policy, which states that existing water uses and the level of water quality necessary to protect the existing uses must be maintained and protected.

Water quality must be maintained and protected unless the state finds that allowing lower water quality is necessary to accommodate important economic or social development in the area in which the water is located. In allowing such degradation or lower water quality, the state must ensure water quality adequate to fully protect existing uses of the water.

The methods of pollution prevention, control, and treatment found to be the most effective and reasonable will be applied to all discharges. All discharges will be treated and controlled to achieve the highest statutory and regulatory requirements for point sources and all cost-effective and reasonable BMPs for nonpoint sources. State water exhibiting high-quality water constitutes an outstanding national resource and must be maintained and protected.

2.4. Designated Use Impacts

Slate Creek was placed on the 2012 section 303(d) list for non-attainment of the freshwater quality criteria for antimony and arsenic (ADEC 2012b). Subsequent data analyses show that iron is also exceeding the water quality criterion (Section 3.2); therefore, iron is also included in this TMDL report. The non-attainment affects the designated uses of (1) water supply, (2) water recreation, and (3) growth and propagation of fish, shellfish, other aquatic life, and wildlife. Restoration efforts (Sections 1 and 1.7) have improved turbidity conditions in the watershed (USEPA 2013); however, Slate Creek does not support its designated uses due to elevated levels of antimony, arsenic, and iron; therefore, TMDLs are presented below for these three metals.

2.5. TMDL Target

The TMDL target is the numeric endpoint that both represents attainment of applicable water quality standards and is used to evaluate the loading capacity and necessary load reductions. Because all designated uses must be addressed unless specifically exempted in Alaska, the TMDL must use the most stringent of the criteria among all of the uses. The TMDL targets for Slate Creek are equivalent to the state drinking water quality criteria of 6 µg/L antimony and 10 µg/L arsenic and the chronic aquatic life criterion of 1,000 µg/L iron. As documented in Section 2.1, these criteria represent the most protective criteria, addressing all designated uses.

The criteria directly address the basis for the antimony, arsenic, and iron impairments and the only known source of impairment, which is the adjacent historic hard rock mine. Sediment quality guidelines (Table 2-3) were also evaluated to determine acceptable levels of metals in the sediment to meet the numeric targets.

3. Data Review

The compilation and analysis of data and information is an essential step in understanding the general water quality conditions and trends in an impaired water. This section outlines and summarizes all of the data reviewed and includes the following information:

- Data inventory—describes the available data and information used to evaluate water quality conditions.
- Data analysis—presents results of various data analyses evaluating trends and relationships in in-stream data.

3.1. Data Inventory

Water quality monitoring has been conducted at Slate Creek since 1982. The United States Fish and Wildlife Service (USFWS) first sampled Slate Creek during a Kantishna Hills heavy metal investigation in the early 1980s. The creek has since been sampled by USGS and researchers at the University of Alaska at Fairbanks (UAF). Six monitoring studies were evaluated that included sampling of various media in Slate Creek focused on metals contamination due to historical mining operations. Relevant reports are listed in Table 3-1. This TMDL report addresses the antimony, arsenic, and iron impairments, but all available data were reviewed for the purpose of confirming existing impairment and identifying any additional impairments.

Table 3-1. Summary of Slate Creek monitoring reports

Report Title	Author(s)	Agency	Publication Date	Data Type for Slate Creek	Years Sampled
Water quality of streams draining abandoned and reclaimed mined lands in the Kantishna Hills area, Denali National Park and Preserve, Alaska, 2008–11	Brabets & Ourso	USGS	2013	Water, Sediment	2008-2011
Mobility and chemical fate of antimony and arsenic in historic mining environments of the Kantishna Hills district, Denali National Park and Preserve, Alaska	Ritchie et al.	University of Alaska	2013	Water, Sediment	2005 and 2007
Environmental-Geochemical Study of the Slate Creek Antimony Deposit, Kantishna Hills, Denali National Park and Preserve, AK	Eppinger et al.	USGS	2000	Water, Sediment	1998
Effects of Mining Disturbances on Stream Invertebrates and Primary Producers in Denali National Park, Alaska	Oswood et al.	University of Alaska	1990	Water	1984
Kantishna Hills heavy metals investigations, Denali National Park, 1983	West & Deschu	USFWS	1984	Water	1983
Kantishna Hills heavy metals investigation: Denali National Park Interagency Agreement 14-16-0007-82-5524	West	USFWS	1983	Water	1982

Monitoring locations for metals and field data collected since 1982 are shown in Figure 3-1 and Figure 3-2. These data at 32 sampling stations have been collected by researchers at University of Alaska at Fairbanks (UAF; Ritchie et al. 2013 [represented by the “Ritchie Sampling Stations” in Figure 3-1]), USGS (Brabets and Ourso 2013 [represented by the USGS Gage in Figure 3-1]), Eppinger et al. (2000 [represented in Figure 3-2]), and USFWS (represented by “West 1982 Sampling Stations” and “West and Deschu Sampling Stations” in Figure 3-1). These data are discussed below in Section 3.2, with a focus on data collected since 2005.

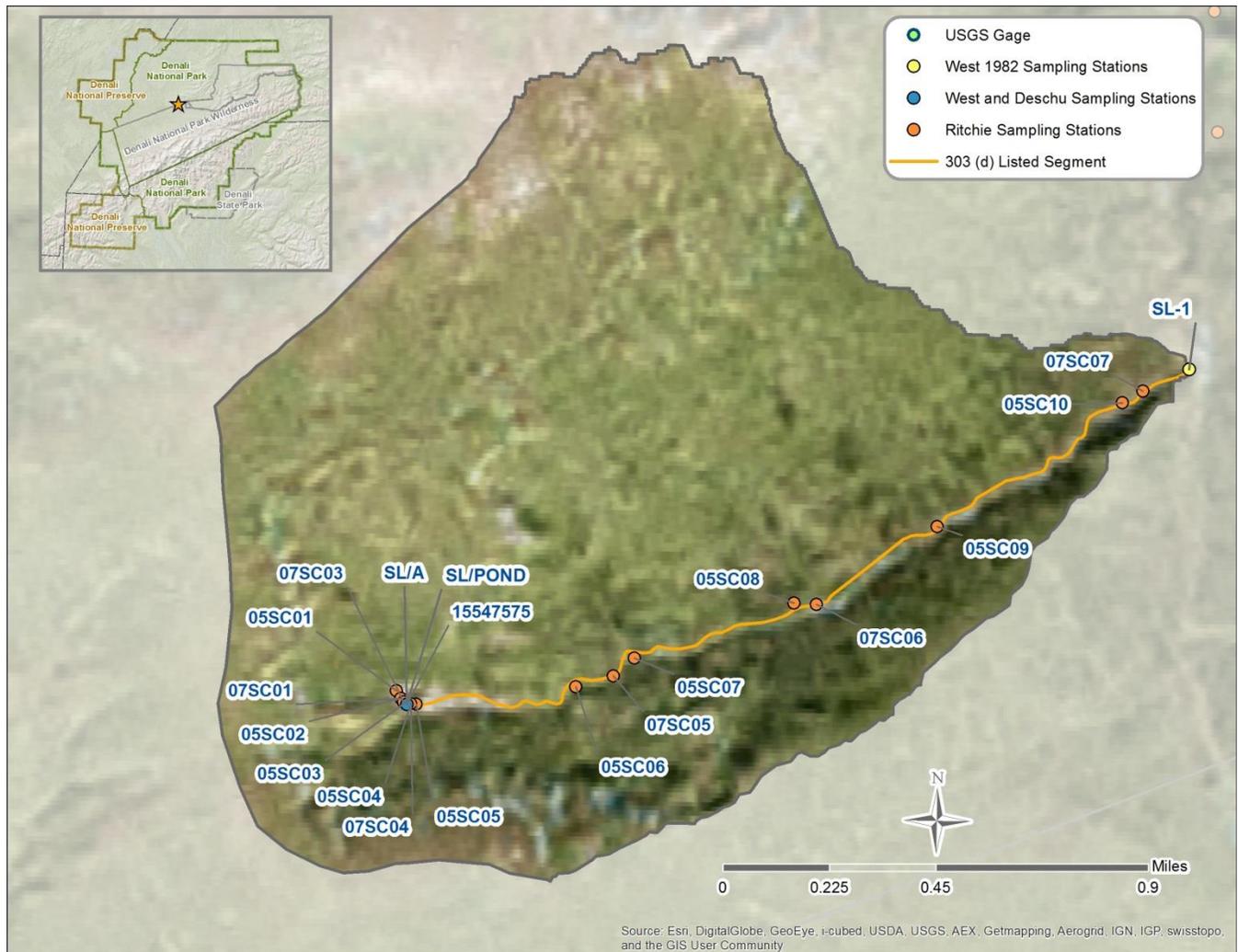


Figure 3-1. Location of 1982-2011 water quality monitoring stations in the Slate Creek watershed.

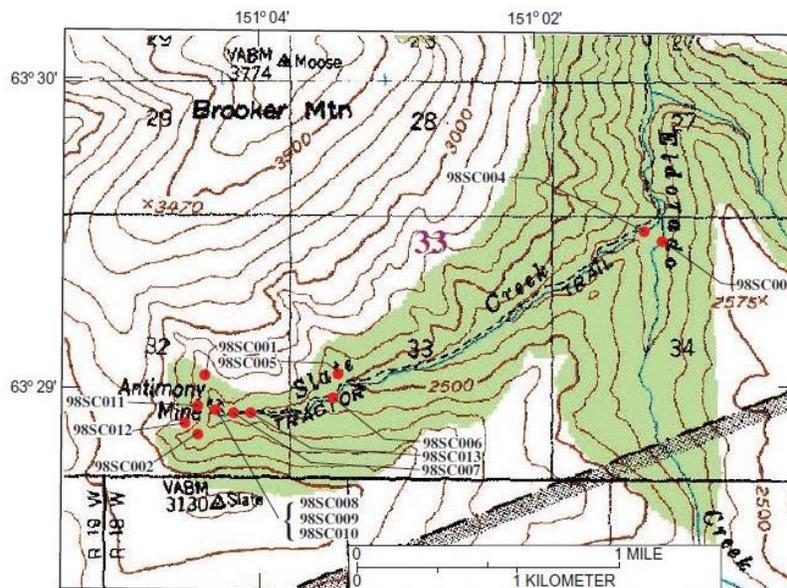


Figure 3-2. Slate Creek antimony deposit, showing locations of sites where samples were collected. Topography from U.S. Geological Survey Mount McKinley 1:63,360-scale topographic maps (Source: Eppinger et al. 2000).

3.2. Data Analysis

The following sections discuss data analyses conducted to evaluate any important trends or impairments of water quality in Slate Creek. Slate Creek monitoring data associated with three time periods were reviewed: pre-restoration (1982 and 1983), during initial restoration (1998), and current conditions (2005 to 2011). Study data before 2005 were not used to characterize conditions in Slate Creek because they were not considered representative of current water quality conditions; however, they are useful to evaluate longer-term trends when compared with more recent data. The various studies are discussed briefly below by time period.

- **1982 and 1983 Surface Water Quality Monitoring:** A single water quality monitoring sample near the Slate Creek mouth was collected in 1982 as part of a greater Kantishna Area watershed study and the sample was analyzed for multiple metals (West 1983). In 1983 a single water quality sample was taken above mining activities on Slate and in a settling pond on Slate Creek for multiple metals. The study noted that antimony, arsenic, mercury, and iron were at levels of concern in Eldorado Creek below the Slate Creek confluence (West and Deschu 1984). Both of these studies were conducted before any restoration efforts on Slate Creek and samples were collected just before all mining ceased in Slate Creek when it became part of Denali National Park and Preserve (USEPA 2013).
- **1998 Surface Water Quality Monitoring:** In 1998 USGS sampled 12 stations from small streams, springs, and from a standing prospect pit pool in the Slate Creek watershed (Figure 3-2; Eppinger et al. 2000). The study measured field parameters and metals in water and sediment samples. Although no samples were found to exceed aquatic life criteria, the study noted that aquatic life in the creek was compromised because no algae and sparse to no vegetation were observed within the entire length of Slate Creek. Eppinger et al. found that nearby, unimpaired, creeks contained abundant algae and their channels were well vegetated; conditions observed in Slate Creek were in stark contrast to these creeks (2000). The study found that stream-sediment, rock, and soil samples from all Slate Creek sites had high anomalous arsenic and antimony contents. This study occurred about the time of the first restoration effort on Slate Creek in 1997-1998, which was initiated to address turbidity concerns.
- **2005 through 2011 Surface Water Quality Monitoring:** Current conditions are best represented by the data from Brabets and Ourso (2013) and Ritchie et al. (2013). Specifically, USGS collected monthly water quality data at a single location just downstream of the historic mine (USGS station 15547575) between June and September from 2008-2011, providing a reasonable temporal representation of water quality conditions at this location. In addition, they also collected one sediment sample during this period (Brabets and Ourso 2013). On the other hand, Ritchie et al. (2013) sampled ten stations along Slate Creek in 2005 and six stations along Slate Creek in 2007 (the year is indicated in Figure 3-1 and Figure 3-3 by the first two characters of the station numbers). This study included both water and sediment (at some, but not all locations) samples. Collectively, these two datasets are useful to describe conditions through time and space in Slate Creek for both water and sediment quality.

The Brabets and Ourso (2013) and Ritchie et al. (2013) data (Figure 3-3) were further explored to identify impairments within Slate Creek. Then for parameters with confirmed impairments, spatial and temporal trends were evaluated. These analyses are described below.

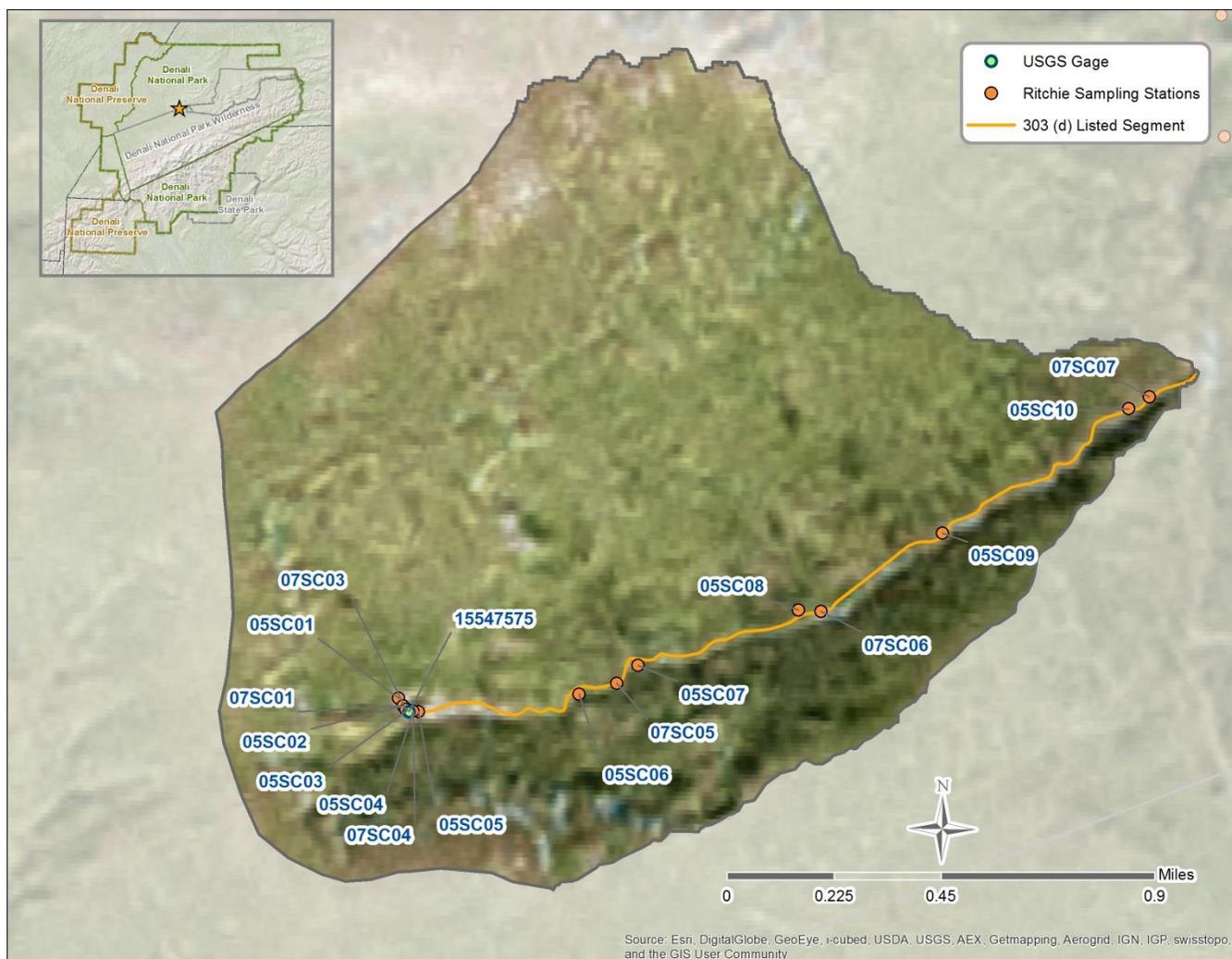


Figure 3-3. Recent sampling stations (2005-2011) on Slate Creek.

3.2.1. Impairment Analyses

Field data (pH, temperature, and dissolved oxygen [DO]) and metals concentrations were compared to applicable water quality criteria to quantify exceedances and identify potential impairments in Slate Creek.

3.2.1.1. Field Data (pH, temperature, and DO)

Table 3-2 and Table 3-3 summarize pH, dissolved oxygen, and water temperature data from Brabets and Ourso (2013) and Ritchie et al. (2013) and compare them to DEC water quality criteria. The first table presents only mainstem stations, while the second table below is associated with tributary and mine waste stations near Slate Creek. All mainstem Slate Creek samples are meeting DEC water quality criteria for DO and temperature (Table 3-2). Dissolved oxygen data were not collected by Ritchie et al. (2013), so the only data for DO are at the USGS station, which are consistently meeting the criterion. There are two pH values at the USGS station that were below the criterion of 6.5 (July 2010 with pH of 6.2 and 6.3 in July 2011); however, when considered with all of the other mainstem samples, these two exceedances out of 27 samples does not suggest an impairment for pH. As shown in Table 3-3, pH data from the mine waste seep and the nearby minor tributary studied by Ritchie et al. (2013) were below the criterion of 6.5. Despite low values at the mine seep and tributary station, these exceedances do not appear to impair the mainstem Slate Creek sites as all pH measurements downstream on the same sample dates were above the pH water quality criterion (Table 3-2, Ritchie Data).

Table 3-2. Summary of mainstem Slate Creek field data

Parameter	Mainstem Slate Creek USGS Data (2008-2011)			Mainstem Slate Creek Ritchie Data (2005 and 2007)	
	pH	Dissolved Oxygen	Water Temperature	pH	Water Temperature
Number of Samples	14	13	13	13	13
Number of Exceedances	2	0	0	0	0
Units (applies to rows below)	pH unit	(mg/L)	(°C)	pH unit	(°C)
Criterion - Minimum	6.5	7.0	N/A	6.5	N/A
Criterion - Maximum	8.5	N/A	20	8.5	20
Average	6.8	10.7	6.1	7.4	8.7
Median	6.7	11.1	6.0	7.3	9.0
Minimum	6.2	8.0	4.0	6.6	4.7
Maximum	7.8	12.5	10.0	8.2	10.4
Standard Deviation	0.4	1.1	1.8	0.5	1.6

N/A = Not applicable; milligrams per liter = mg/L; degrees Celsius = °C

Table 3-3. Summary of Slate Creek tributary and mine waste seep field data

Parameter	Minor Tributary Data (2005)		Mine Waste Seep Data (2005 and 2007)	
	pH	Water Temperature	pH	Water Temperature
Number of Samples	1	1	2	2
Number of Exceedances	1	0	2	0
Units (applies to rows below)	pH unit	(mg/L)	pH unit	(°C)
Criterion - Minimum	6.5	N/A	6.5	N/A
Criterion - Maximum	8.5	20	8.5	20
Average	N/A	N/A	4.2	11.5
Median	N/A	N/A	4.2	11.5
Minimum	6.1	10.7	2.8	11.0
Maximum	N/A	N/A	5.6	12.0
Standard Deviation	N/A	N/A	2.0	0.7

N/A = Not applicable

3.2.1.2. Metals Data

Table 3-4 summarizes surface waters metals data for antimony, arsenic, iron, lead, silver, and zinc, which were the primary mining products extracted from the larger Kantishna Hills area (no gold data were available for analysis). Data were compared to the DEC water quality criteria. No silver exceedances were observed, and lead and zinc exceedances were limited to one mine waste seep sample (not on Slate Creek itself). Twenty-eight antimony, arsenic, and iron samples were available for analysis and all three had a significant number of exceedances (27, 14, and 16, respectively). The maximum values for all metals other than antimony were associated with the mine waste seep station. Antimony showed the highest exceedances when compared with the criteria, while the magnitude of exceedances was lower for arsenic and iron (Table 3-4 and illustrated in Figure 3-4, Figure 3-9, and Figure 3-14 below).

Table 3-4. Surface water metals data summary (2005, 2007, and 2008-2011)

Criteria	Water					
	Antimony	Arsenic	Iron (Dissolved)	Lead (Dissolved)	Silver (Dissolved)	Zinc (Dissolved)
Number of Samples	28	28	28	19	19	28
Number of Exceedances	27	14	16	1 ^a	0	1 ^a
Units (applies to rows below)	(µg/L)					
Drinking/Stock/Irrigation	6	10	5,000	50	N/A	2,000
CCC	N/A	150	1,000	2.52	N/A	118.14
CMC	N/A	340	n/a	64.58	3.22	117.18
Average	263	23	9,437	0.72	1.07	79
Median	186	11	1,215	0.08	2.00	13
Minimum	4	3	39	0.05	0.01	3
Maximum	720	180	218,500	11.00	2.00	1,765

Notes: N/A = Not applicable; ^a = Exceedance was in tailing seep; bold = criterion value used for exceedance assessment; italicized = hardness dependent criteria, value based on hardness = 100mg/L, which is the low end of observed hardness values (a conservative assumption).

Table 3-5 summarizes sediment metals data for antimony, arsenic, iron, lead, silver, and zinc. Data were compared to sediment quality guidelines, where available and applicable. Arsenic and lead exceeded the TEL in 2005 and 2008, while zinc data only exceeded the TEL in 2005. The lead and zinc exceedances in sediment do not appear to be impacting water quality in the creek, demonstrated by the lack of exceedances in the mainstem creek water (Table 3-4).

Table 3-5. Sediment metals data summary (2005 and 2008)

Criteria	Sediment					
	Antimony	Arsenic	Iron	Lead	Silver	Zinc
Number of Samples	11	11	11	11	11	11
Number of Exceedances	n/a	11	N/A	10	N/A	9
Units (applies to rows below)	(mg/kg)					
TEL	N/A	5.90	N/A	35	N/A	123
PEL	N/A	17.00	N/A	91.3	N/A	315
Average	3,974	2,810	157,918	86	2	306
Median	3,890	2,650	118,000	89	2	236
Minimum	116	855	90,400	14	1	92
Maximum	7,230	3,980	406,000	154	2	632

Notes: N/A = Not applicable; bold = criterion value used for exceedance assessment

3.2.1.3. Impairment Summary

Based on the review of available field data and metals concentrations, the primary pollutants of concern are antimony, arsenic, and iron. These three metals demonstrate consistent exceedances in the mainstem of Slate Creek; therefore, these impairments are addressed by this TMDL document. Data associated with antimony, arsenic, and iron (Brabets and Ourso 2013; Ritchie et al. 2013) are further explored in Section 3.2.2 below through the use of temporal and spatial analyses.

3.2.2. Temporal and Spatial Variation of Impairments

Detailed data analyses were performed on more recent data (Figure 3-3). These analyses include temporal and spatial assessments using the data identified below:

- Temporal analyses: based on data collected over time at a single point in the watershed using the USGS data and stations 05SC04 and 07SC04 of the UAF data, which are located in close proximity to the USGS station (Brabets and Ourso 2013; Ritchie et al. 2013);
- Spatial assessments: using the Ritchie et al. (2013) data collected along the entire length of Slate Creek representing the entire impaired reach (Figure 3-3).

Results are presented by parameter in the sections below for antimony, arsenic, and iron, which were identified as the impaired pollutants (Section 3.2.1).

3.2.2.1. Antimony

Antimony data in Slate Creek exceeded the drinking water criteria of 6 µg/L in all but one headwater sample in 2005. Figure 3-4 displays the antimony data located near USGS gage 15547575 from 2005 to 2011 to evaluate variations through time (note, these include two stations from Ritchie et al. [2013] that are located just downstream of the USGS station). Surface water antimony levels near USGS gage 15547575 do not appear to have changed much over time ranging from 89 to 446 µg/L with the highest observed antimony levels in July 2007 (Station 07SC04; 0.1 km from the headwaters) and July 2009 (Station 15547575; 0.06 km from the headwaters). There were not enough data to perform a monthly temporal analysis to evaluate seasonal variations. Ultimately, the central tendency of the data is around 150 µg/L, well above the drinking water criterion (Figure 3-4).

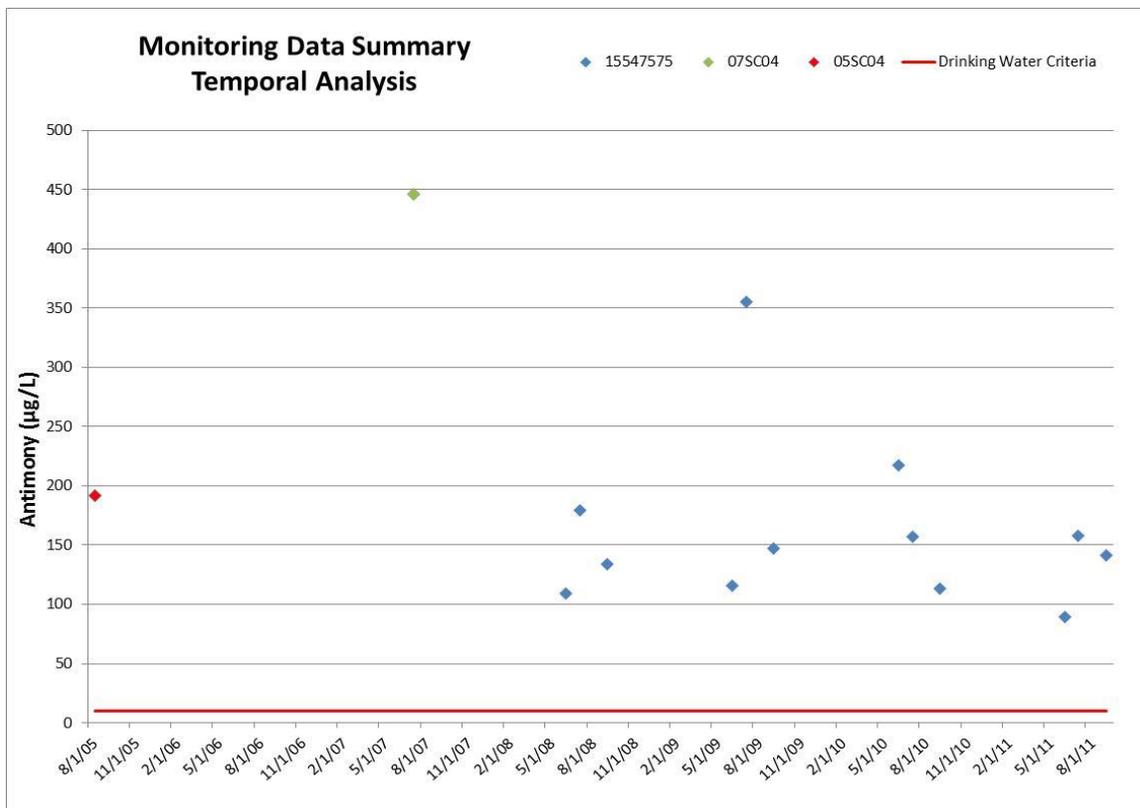


Figure 3-4. Temporal analysis of water antimony data at mainstem Slate Creek stations 15547575, 05SC04 and 07SC04 from 2005 to 2011.

Antimony data were analyzed for spatial patterns in 2005, 2007, and all years in Figure 3-6, Figure 3-7, and Figure 3-8, respectively, and the stations are represented visually in Figure 3-5. In both 2005 and 2007, antimony water levels were lowest in the headwaters and rose below the mine tailing waste seep before decreasing slightly near the mouth at Eldorado Creek. Sediment levels of antimony appeared to follow this same pattern in 2005. In

2005, antimony water levels from the mine water seep and a minor tributary were much higher than those in the headwaters, though in 2007 antimony levels in the mine waste seep water were slightly lower than those observed in the headwaters (no data were available for the tributary in 2007). Levels of antimony in the sediment samples increased from 1,040 mg/kg in the mine waste seep to almost 5,000 mg/kg downstream of the seep at 05SC04 in 2005.

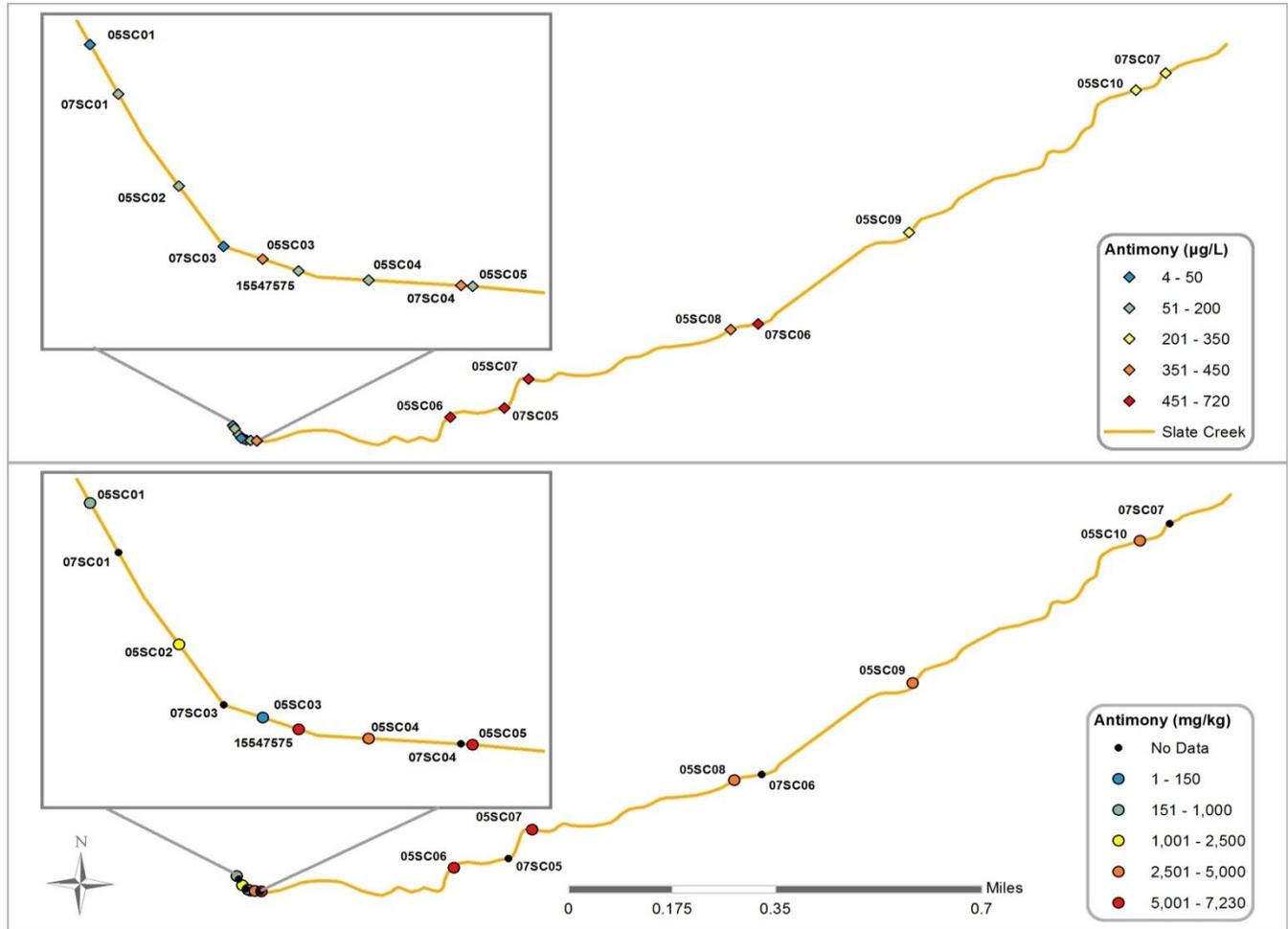


Figure 3-5. Spatial map of antimony data from 2005 to 2011 for water (top panel) and sediment (bottom panel).

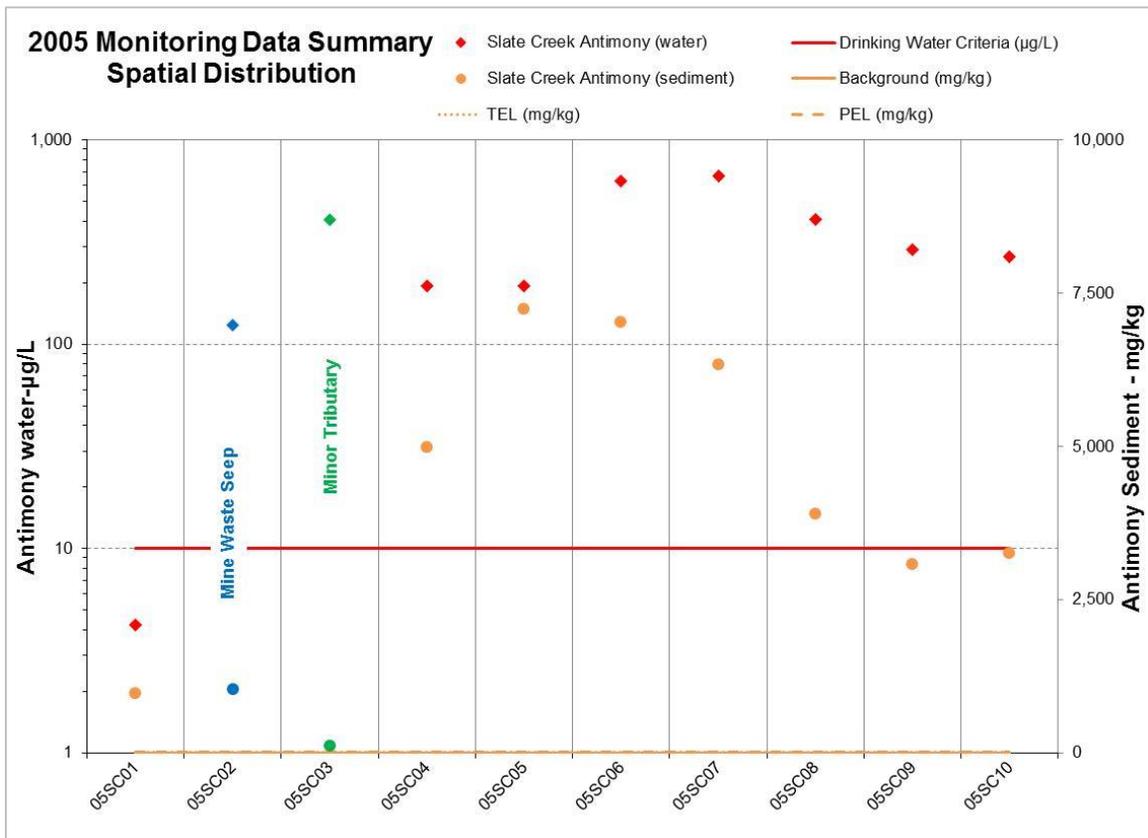


Figure 3-6. Spatial analysis of 2005 water and sediment Slate Creek antimony data.

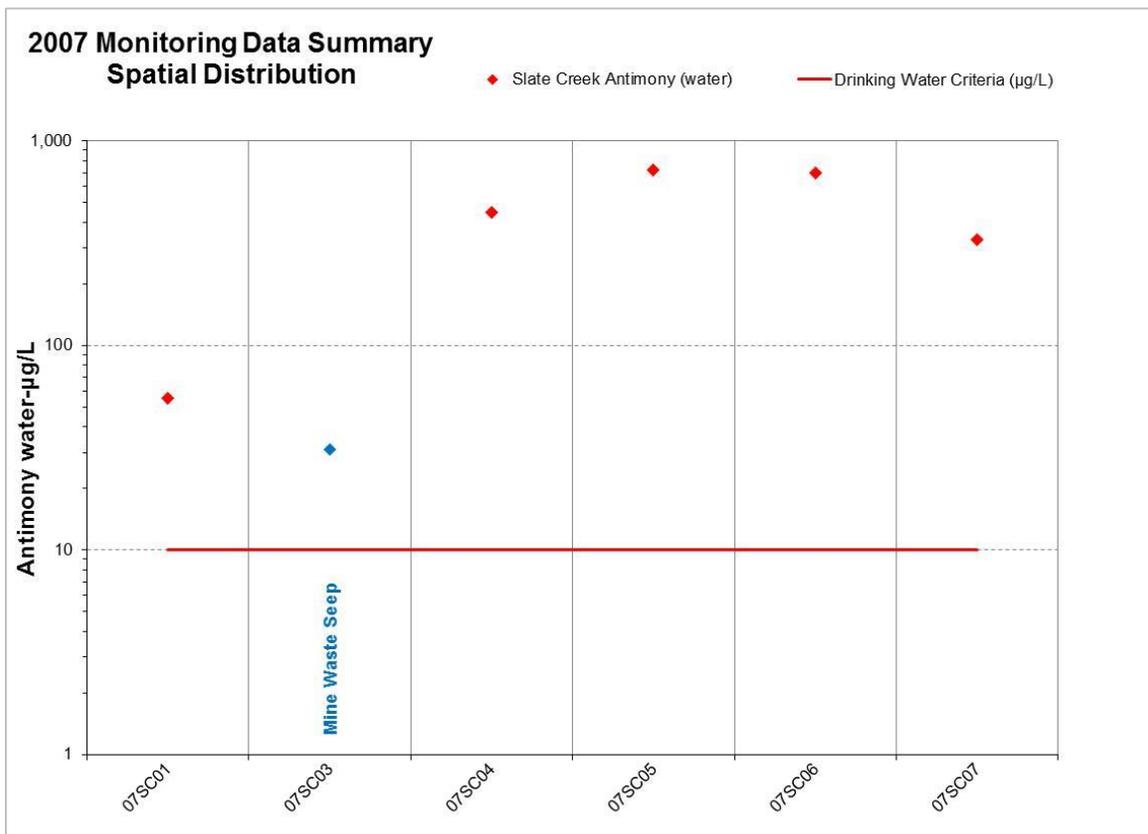


Figure 3-7. Spatial analysis of 2007 water Slate Creek antimony data.

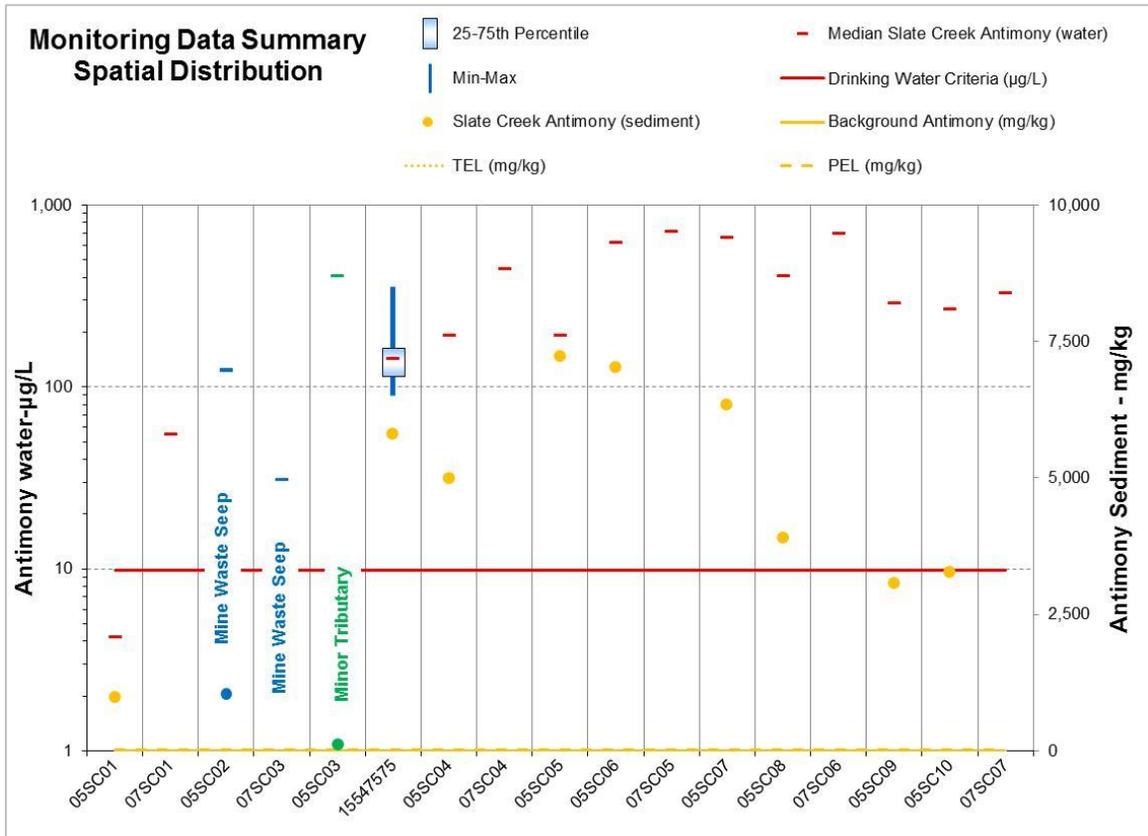


Figure 3-8. Spatial analysis of water and sediment Slate Creek antimony data.

3.2.2.2. Arsenic

Arsenic data in Slate Creek exceeded the drinking water criteria of 10 µg/L in 14 of 28 samples analyzed from 2005 to 2011. Figure 3-9 displays the arsenic data near USGS gage 15547575 from 2005 to 2011 to evaluate conditions through time. Surface water arsenic levels near USGS gage 15547575 appear to be increasing over time, likely because the iron concentrations show a similar pattern and arsenic has a strong affinity for iron. From 2005 to 2009 arsenic levels were below 20 µg/L at stations 05SC04 (0.07 km from the headwaters), 07SC04 (0.1 km from the headwaters), and 15547575 (0.06 km from the headwaters). In 2010 and 2011, all arsenic samples were above 20 µg/L with the highest observed arsenic concentrations measured in July and September of 2011.

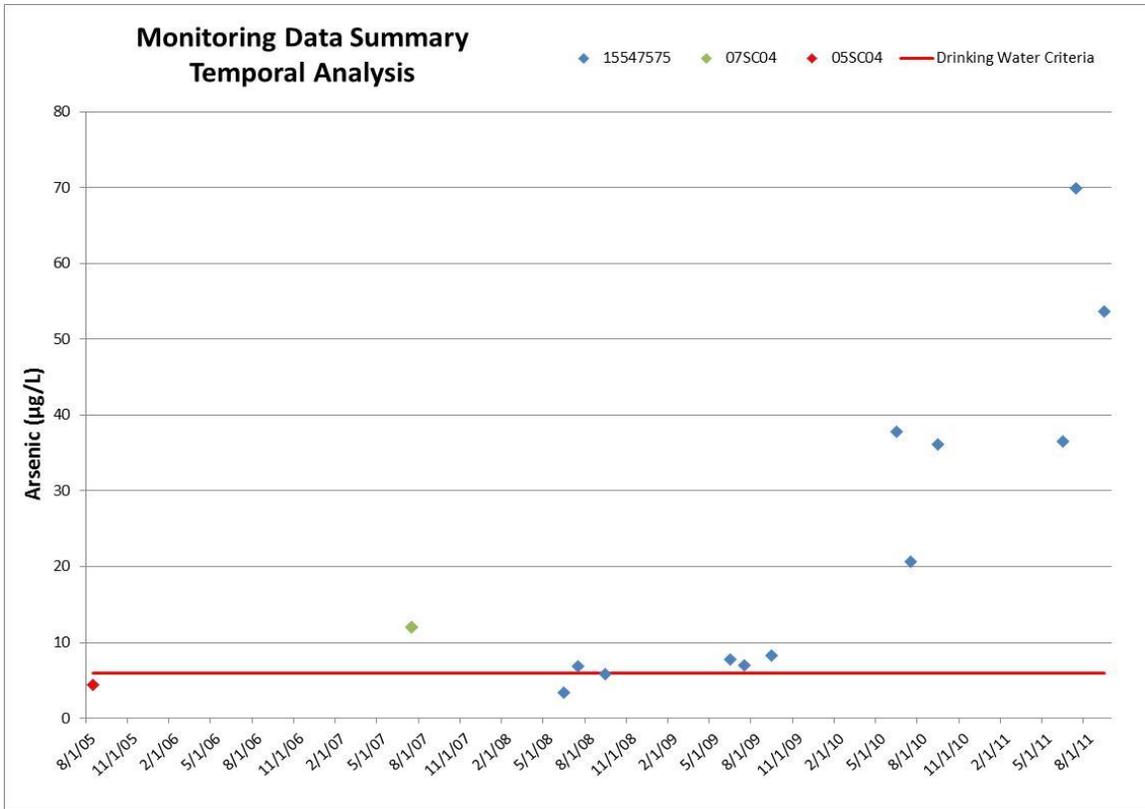


Figure 3-9. Temporal analysis of water arsenic data at mainstem Slate Creek stations 15547575, 05SC04 and 07SC04 from 2005 to 2011.

Arsenic data were analyzed for spatial patterns in 2005, 2007, and in all years in Figure 3-11, Figure 3-12, and Figure 3-13, respectively, and the stations are represented visually in Figure 3-10 to illustrate the spatial distribution. In 2005, consistent with the results for antimony, arsenic water levels were lowest in the headwaters and rose below the mine tailing waste seep before decreasing near the mouth at Eldorado Creek. Both surface water and sediment levels of arsenic were high in the mine waste seep with sediment levels increasing downstream to 05SC05 before starting to decrease again moving towards the mouth near Eldorado Creek. Similarly, water concentrations increased to 05SC06 before decreasing again moving downstream. In 2007, arsenic water levels were lowest in the headwaters, rose below the mine tailing waste seep, and then decreased near the mouth at Eldorado Creek. The mine waste seep had the highest observed surface water arsenic concentration (180 µg/L) though sediment concentrations of arsenic were higher downstream from the seep.

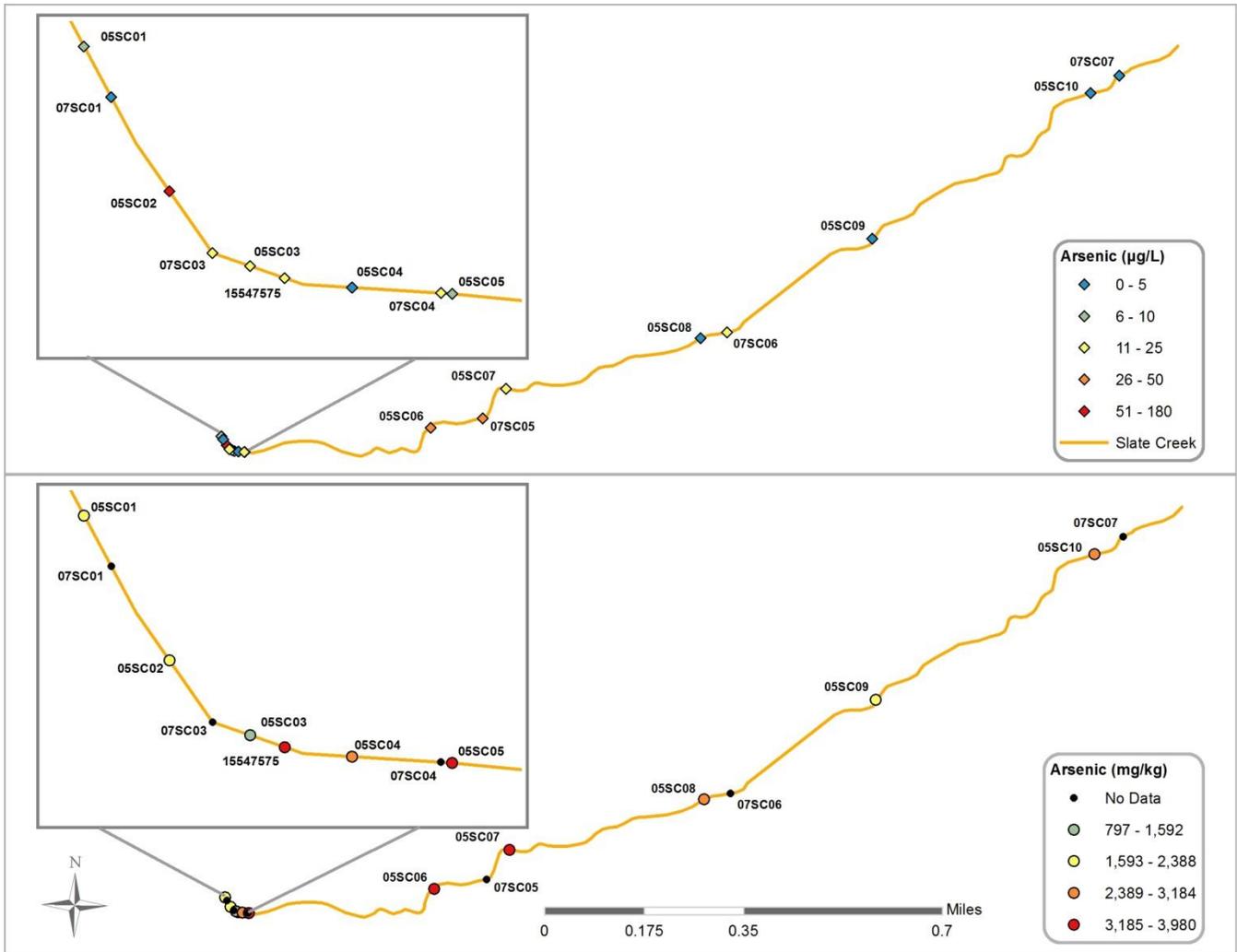


Figure 3-10. Spatial map of arsenic data from 2005 to 2011 for water (top panel) and sediment (bottom panel).

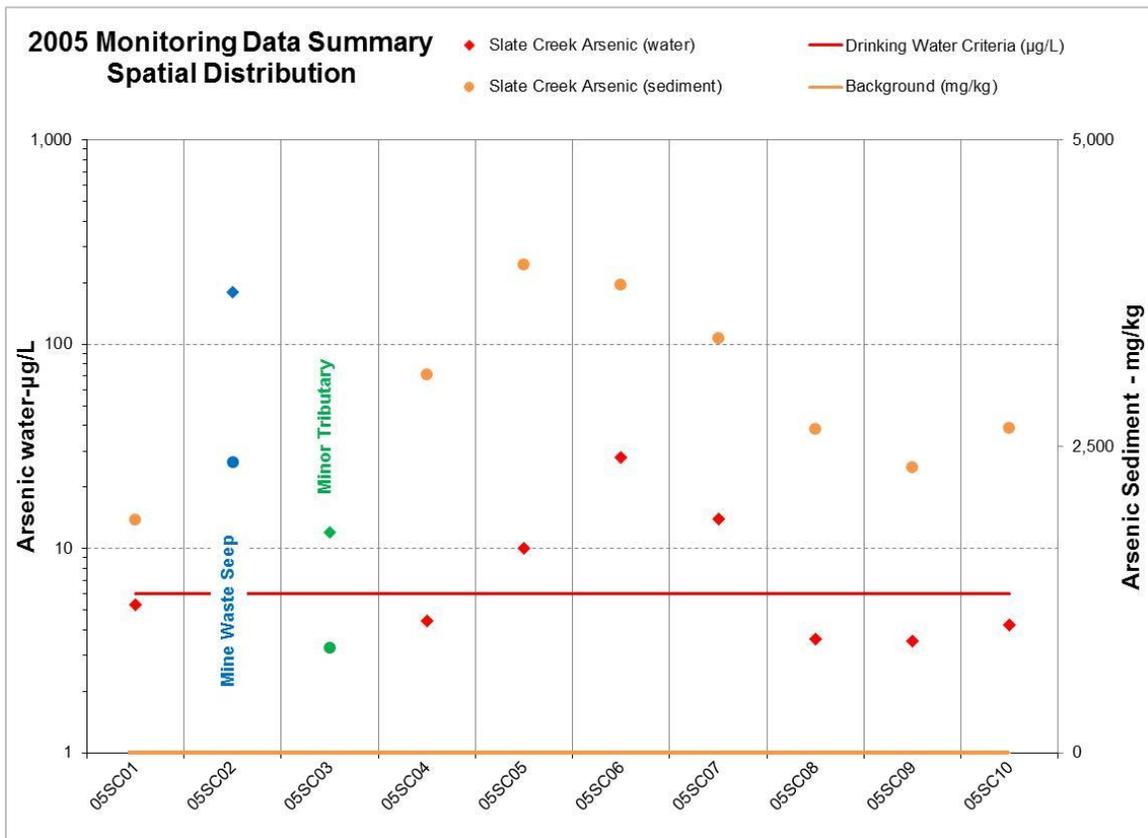


Figure 3-11. Spatial analysis of 2005 water and sediment Slate Creek arsenic data.

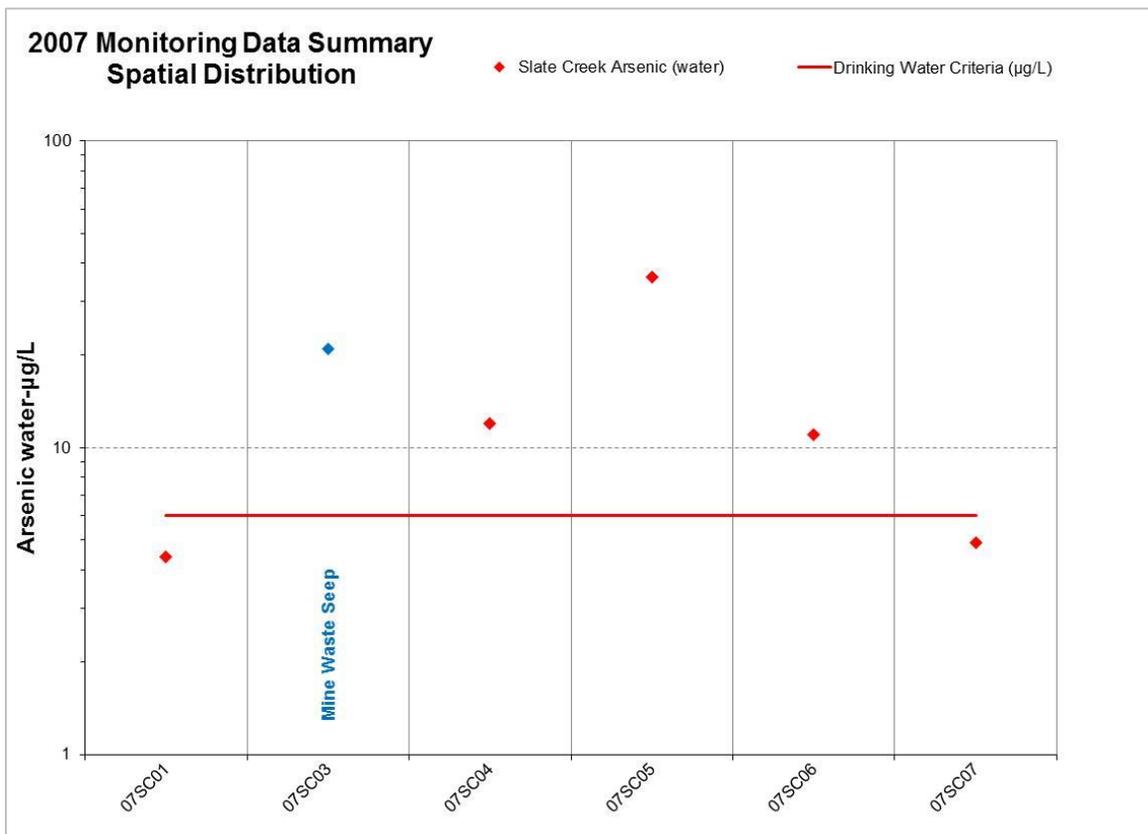


Figure 3-12. Spatial analysis of 2007 water Slate Creek arsenic data.

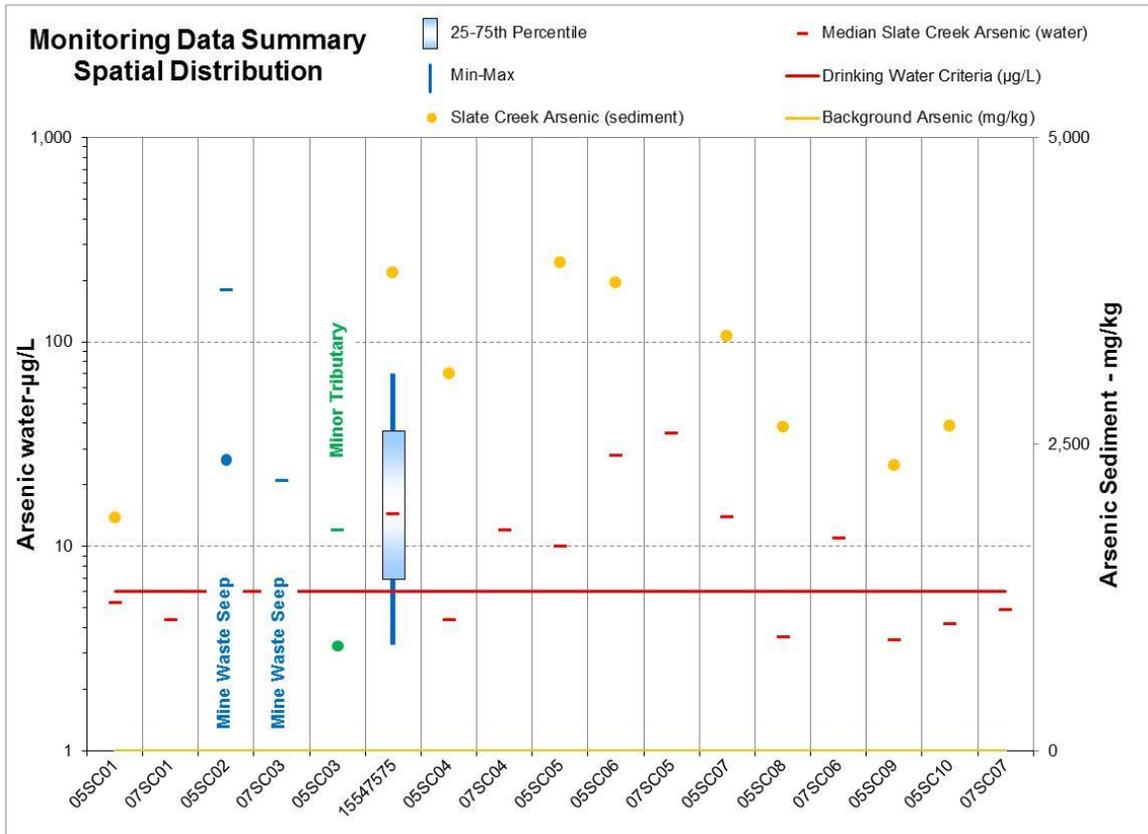


Figure 3-13. Spatial analysis of water and sediment Slate Creek arsenic data.

3.2.2.3. Iron

Iron data in Slate Creek exceeded the chronic aquatic life criteria of 1,000 µg/L in 16 out of 28 samples. Figure 3-14 displays the iron data near USGS gage 15547575 (including two nearby stations from the Ritchie et al. [2013] study) from 2005 to 2011 to evaluate temporal patterns. The sampling results near USGS gage 15547575 were highly variable, ranging from 323 to 2,980 µg/L. The highest observed iron levels were measured in July of 2009 and 2011 and September of 2011 (Station 15547575; 0.06 km from the headwaters). There were not enough data to perform a detailed monthly temporal analysis, though it appears that iron values in June are typically lower than those in July and September from 2008 to 2011, while the most recent measurements were higher than the previous concentrations. The monthly differences may be due to higher stream temperatures in the later summer months. Specifically, higher temperatures ultimately lead to more reducing conditions in the stream; thereby, increasing the dissolved fraction in the water column. Conclusions on the overall increasing temporal pattern cannot be made because sediment data are not available for multiple years and the water concentrations are closely linked to sediment concentrations.

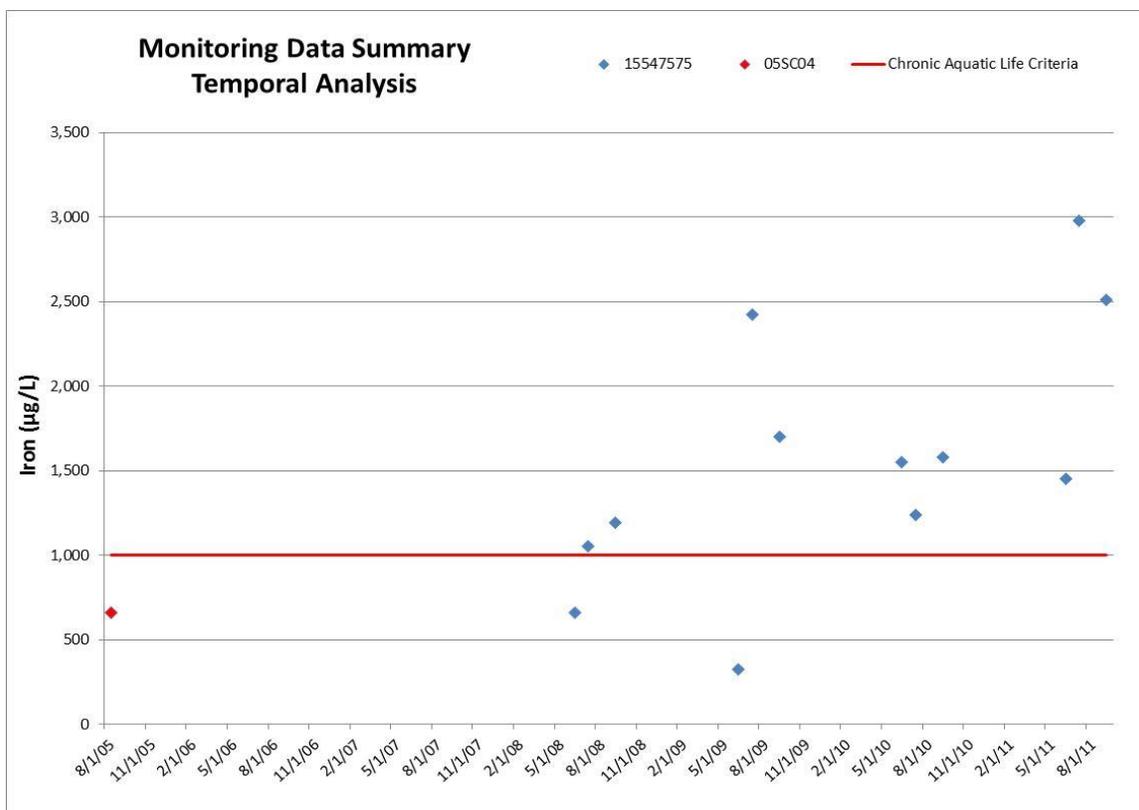


Figure 3-14. Temporal analysis of water iron data at mainstem Slate Creek stations 15547575 and 05SC04 from 2005 to 2011.

Iron concentrations were also analyzed for spatial patterns and mapped in Figure 3-15. Spatial results for 2005, 2007, and all years are presented in Figure 3-16, Figure 3-17, and Figure 3-18, respectively. In both 2005 and 2007, iron water levels were lowest in the headwaters and rose below the mine tailing waste seep before decreasing below the water quality criterion near the mouth at Eldorado Creek. Sediment levels of iron appeared to follow this same pattern in 2005 though they increased slightly near the mouth. In 2005, iron water and sediment levels from the mine water seep and a minor tributary were much higher than those in the headwaters and downstream.

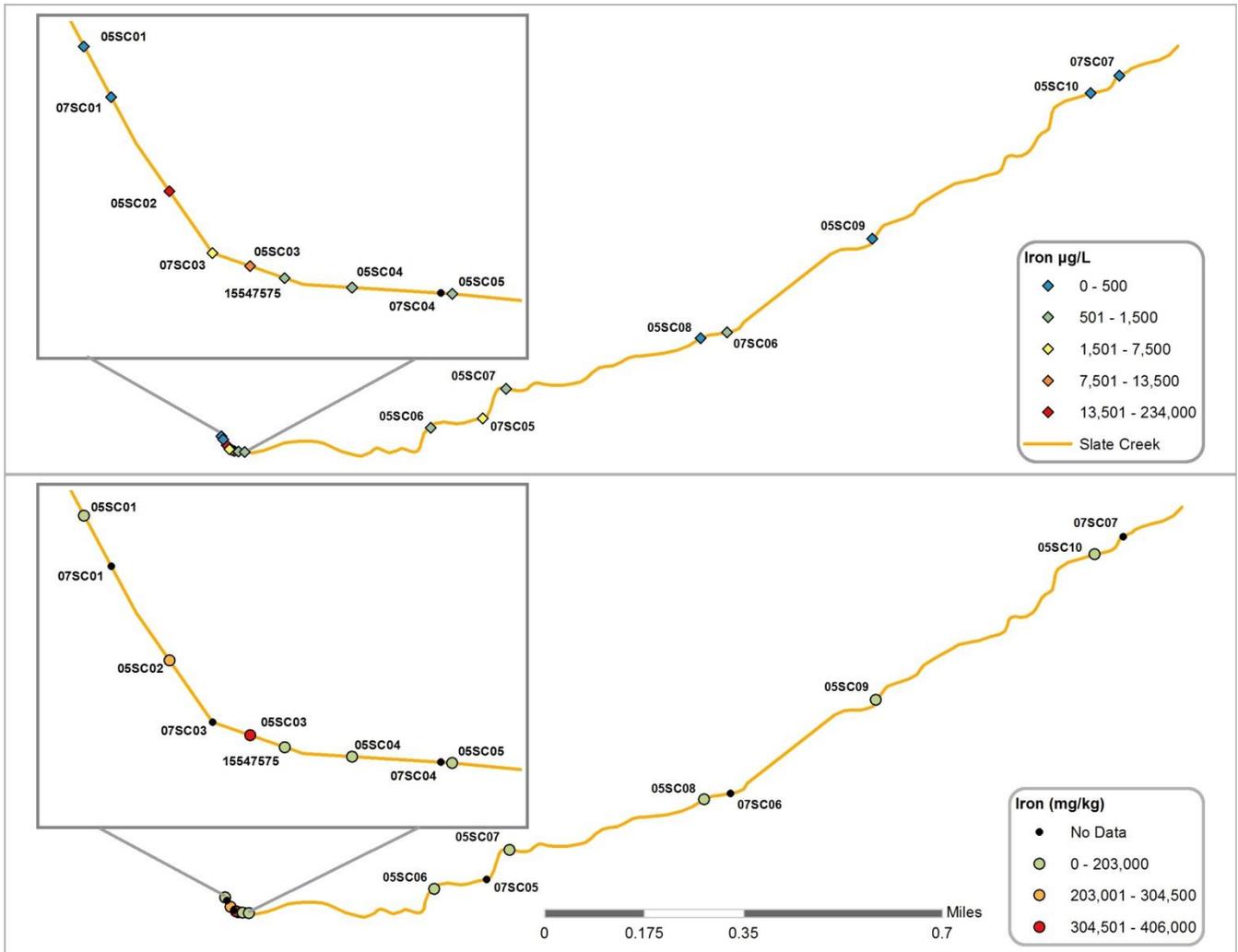


Figure 3-15. Spatial map of iron data from 2005 to 2011 for water (top panel) and sediment (bottom panel).

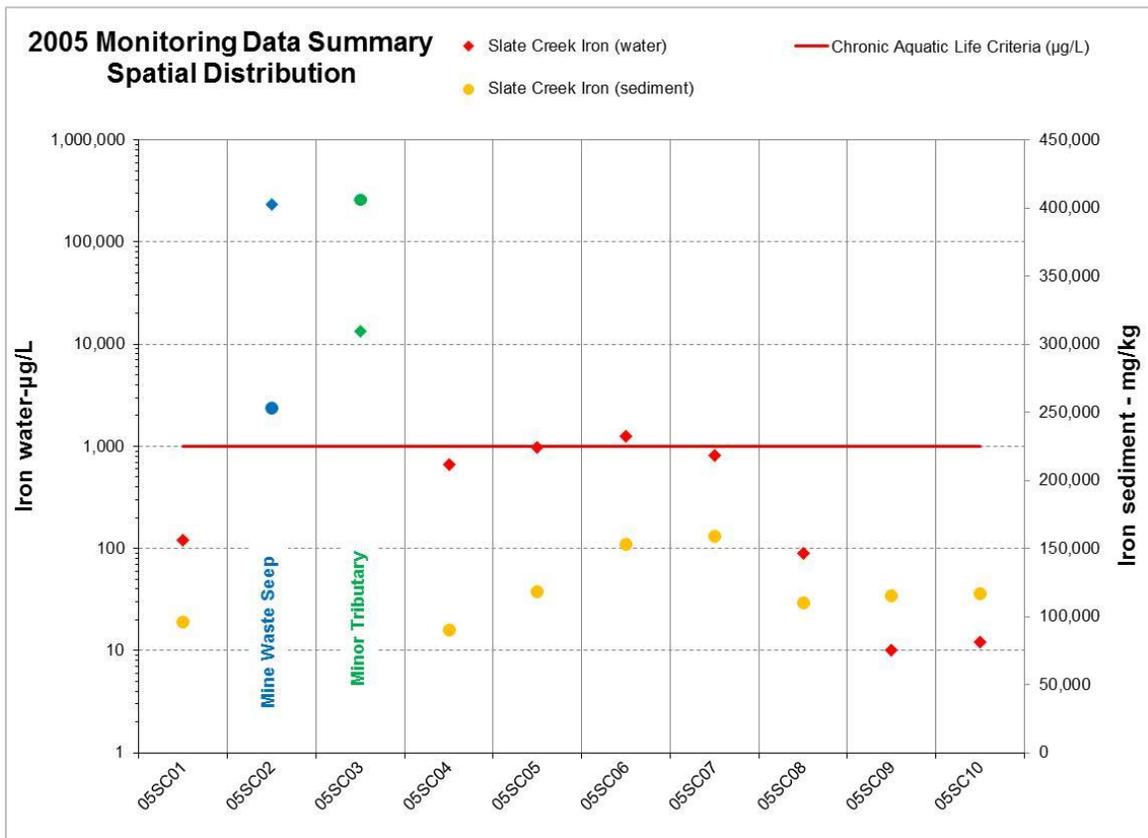


Figure 3-16. Spatial analysis of 2005 water and sediment Slate Creek iron data.

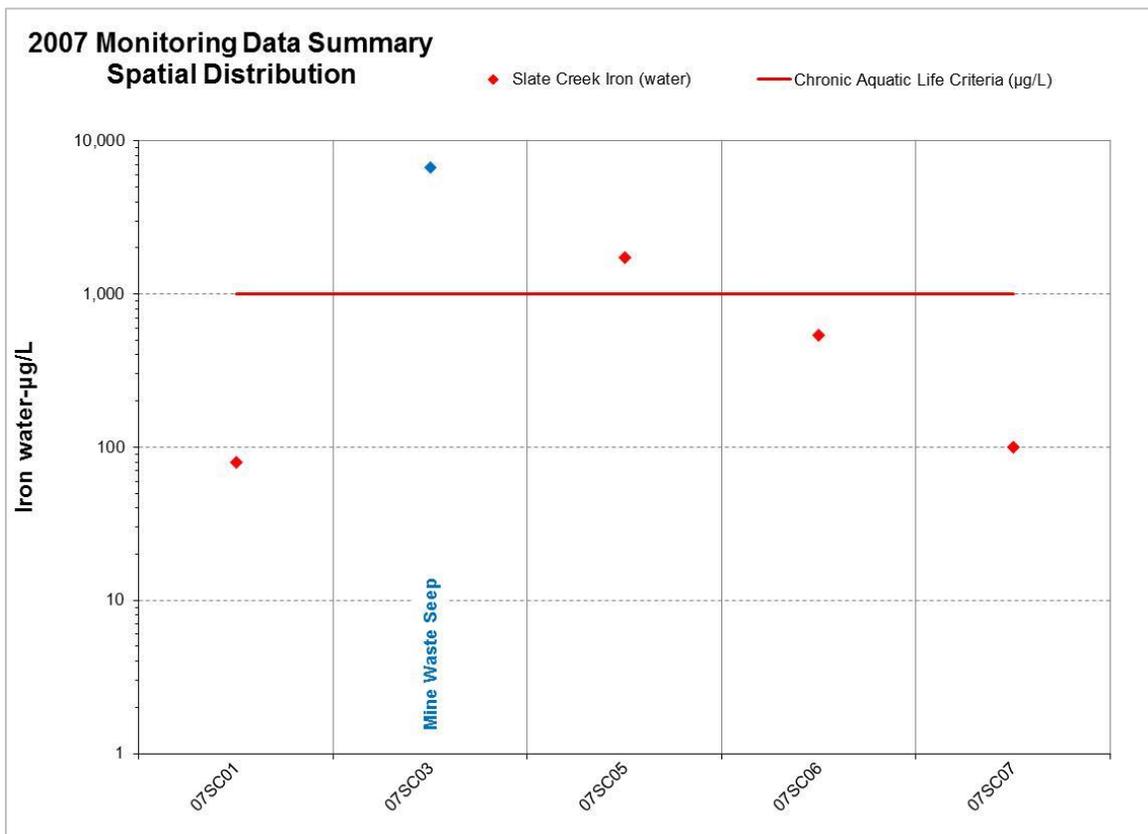


Figure 3-17. Spatial analysis of 2007 water Slate Creek iron data.

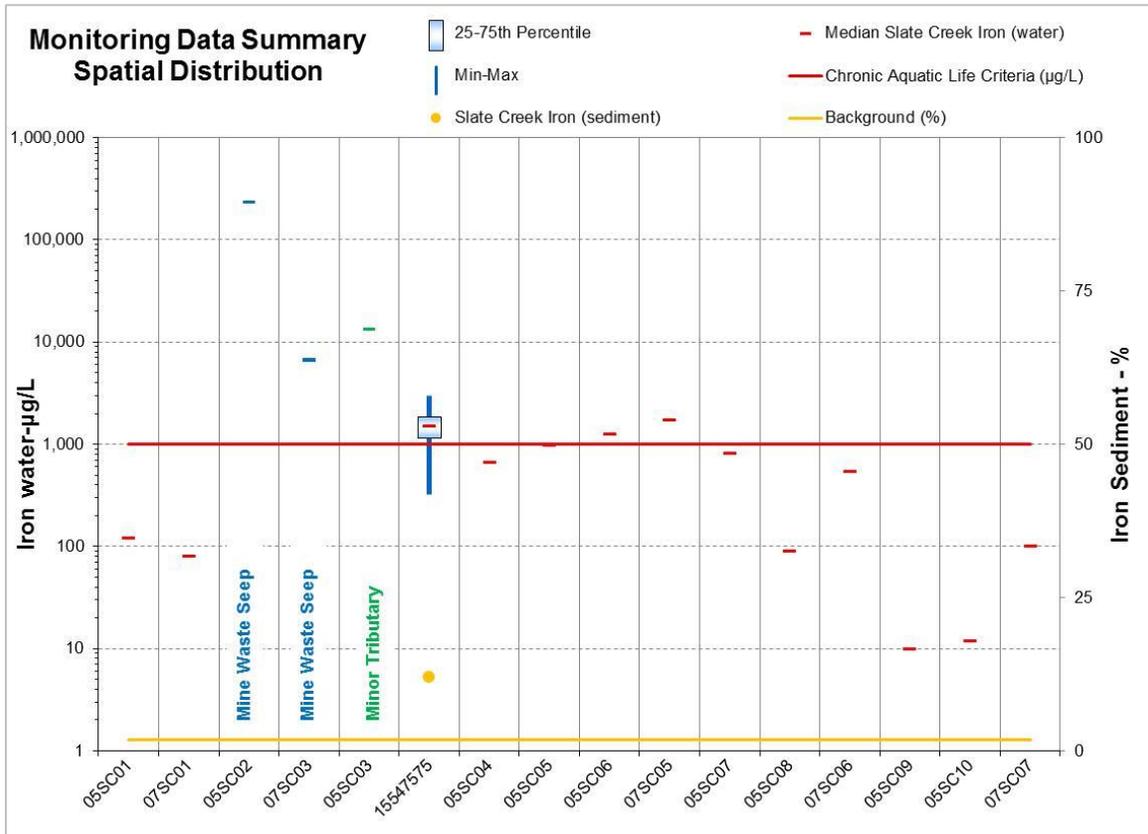


Figure 3-18. Spatial analysis of water and sediment Slate Creek iron data.

4. Supplemental Analysis of Water and Sediment Quality

The USGS's pH-Redox-Equilibrium-Equations in C and C++ Model (PHREEQC model; Parkhurst and Appelo 2013) was selected to evaluate iron, arsenic and antimony's fate and transport in Slate Creek and to support TMDL analyses. PHREEQC is a computer program used to simulate chemical reactions and transport processes in a waterbody. Considering the potential sediment contribution of antimony, arsenic, and iron between the sediment and water interface, the reactions and functionalities included in the model are appropriate for this modeling study. The modeling output reflects the various metals sources, including the mining-affected area, tailing piles, and the potential effects from the upstream sediments. This section provides an overview of the modeling study, model results including load reduction scenarios, and applicability of the model to these TMDLs. Details on the model are provided in Appendix A.

4.1. Modeling Methodology

The model was configured to represent the system hydraulics and water quality using the available data and information to ensure that system hydrology and pollutant loading are characterized as accurately as possible.

The Slate Creek model was configured to represent eight model segments. The segmented locations were based on the available water quality data along Slate Creek. Figure 4-1 shows the water quality sampling locations (e.g., 05SC01; see Figure 3-3 for a map with these locations) with the identified external sources and the river meter associated with the model segment in parentheses. Flow and water quality inputs to the system were then represented using boundary conditions. Specific inputs included the headwaters, mine waste seep, tributary, tailing piles, and other diffuse sources.

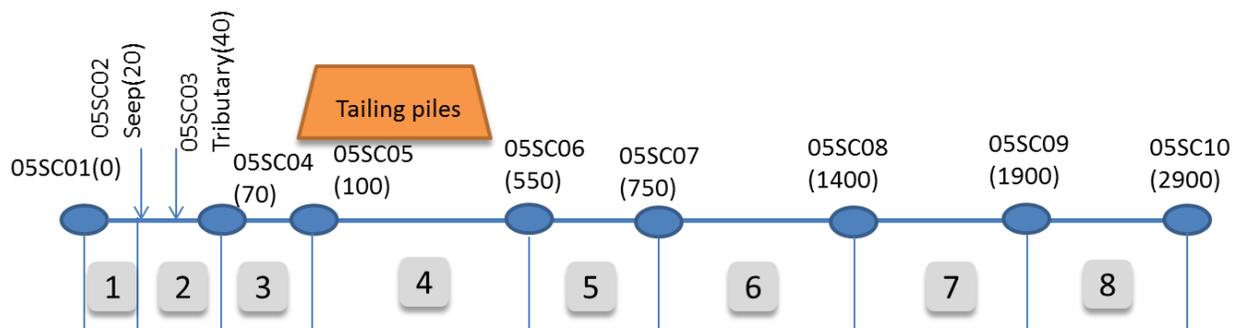


Figure 4-1. Slate Creek model segments.

The PHREEQC model considers many interactions and reactions to simulate water chemistry. Some of the key processes that drive conditions within Slate Creek include in-stream processes, sediment processes, and iron sediment conditions. Appendix A provides details on the model representation of these processes.

4.2. Model Results

Model simulation results are shown below and compared to the observed data (Figure 4-2). Although limited data were available from the sites for comparison, results indicate that the model assumptions and selected parameters described in the previous sections reasonably represent the conditions in Slate Creek, when comparing all parameters below and especially arsenic, antimony, and iron (Figure 4-2). Other simulation results were also provided to evaluate the ability of the model to represent the water quality conditions and the selected source mixing ratio.

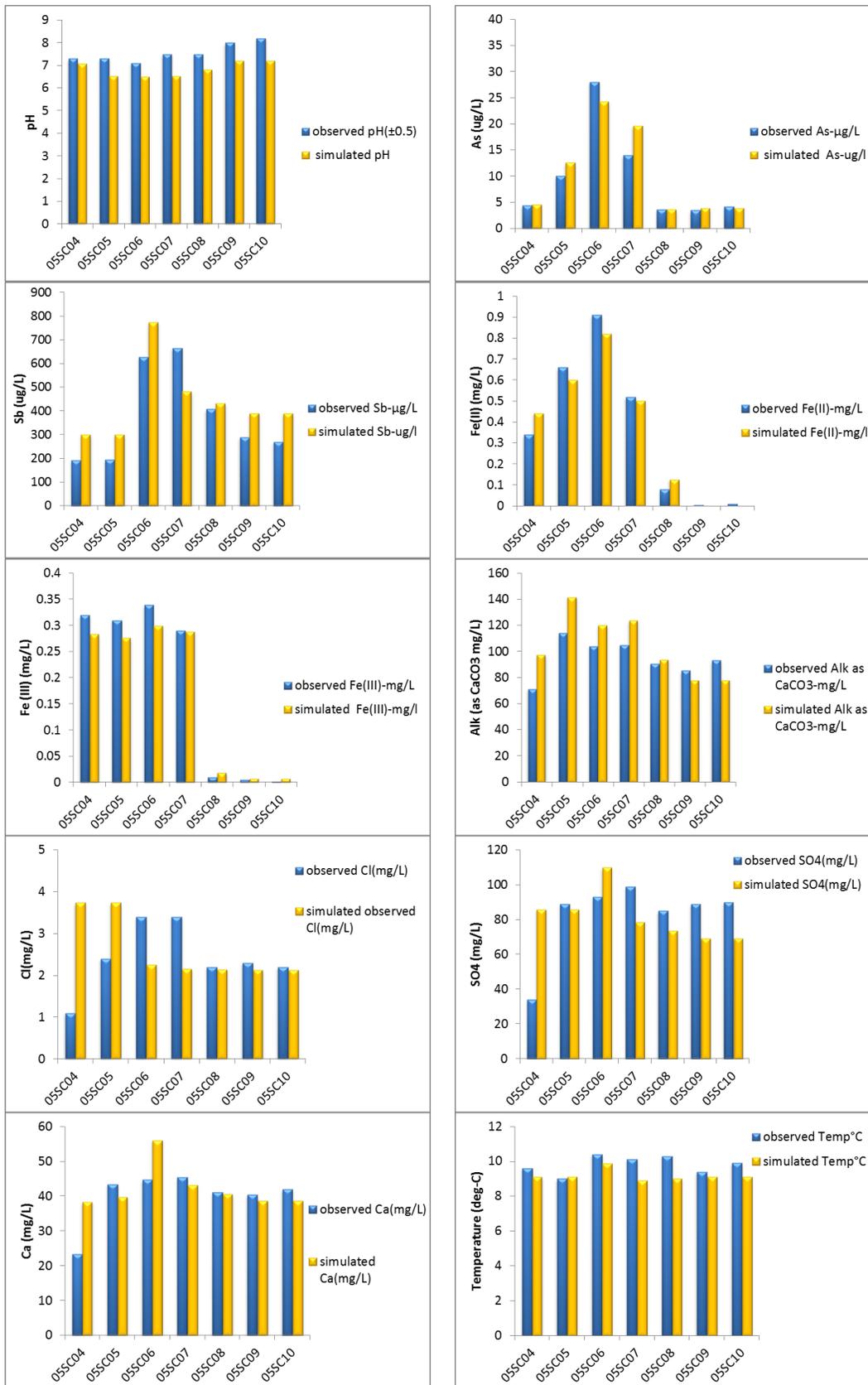


Figure 4-2. Comparison of modeled and observed water quality parameters.

4.2.1. Scenarios to Meet TMDL Numeric Targets

After confirming the good agreement of the model results with the observed data (Figure 4-2), remediation scenarios were simulated to identify the necessary measures to meet the TMDL numeric targets of 6 µg/L antimony, 10 µg/L arsenic, and 1,000 µg/L iron (Section 2.5).

Iron reductions were initially simulated because many other metals show an affinity to iron; therefore, reductions in iron are expected to result in reduced concentrations of other metals. Arsenic and antimony reduction scenarios were subsequently conducted (although the order of these two scenarios is less important). Arsenic has a higher affinity to iron than antimony, so the iron reductions play a larger role in achieving water quality criteria for arsenic. The methodology applied for the reduction scenarios is described below.

1. **Iron:** Iron reductions were initially targeted in the modeling scenarios. According to the observed data and the simulated results, only stations 05SC05 and 05SC06 exceeded the iron water quality criterion. In this scenario, the commonly used remediation chemical, calcite (CaCO_3), was applied to neutralize net acidity to promote ferric iron oxidation and precipitation. In the end, 2 mg/L at 05SC04 and 05SC05, 3 mg/L at 05SC06 of calcite were needed to reduce the total iron to meet the criterion throughout the waterbody. The required daily calcite dosage for the reduction was calculated to be 83 pounds per day.

The described alkaline dosage promotes iron precipitation in the solution at each segment to meet the criterion. However, if there is no source control and the alkaline addition is terminated, transported iron load from the known sources (seep, tributaries, tailings, etc.) would maintain high iron concentration in the creek. If removals of the mining wastes are not feasible, additional remediation measures such as capping and/or lining (see Section 7.1) would be necessary. Even after hydrologic connectivity is disconnected by capping, pore solution between the sources and the creek could contain the high pre-remediated iron concentration. The subsurface high iron content could negate the remediation effort for some period; thus, require the continuous alkaline dosage until background solution (with lower iron content) replace the pre-remediated solution. Therefore, it is critical to identify residence time of the subsurface solution to determine the dosing duration.

To assess residence time, the subsurface velocity was estimated. Subsurface soil was assumed to consist primarily of sandy-loam size soils based on the SSURGO data. Using water filled sand-loam porosity (0.3) with a hydraulic gradient estimated from the topographical slope (0.01), the velocity was calculated to be 396 feet per year. The majority of the physical location of the tailings and sources appear to exist within close proximity (less than 400 feet) or adjacent to the creek. According to topographic maps, the distance from the mining area to the affected stream reach was estimated to be around 160 feet. Considering this information, it was concluded the pre-remediated solution could potentially drain to the creek approximately within 150 days.

Additional analyses were conducted on iron sediment aging related to iron dissolution from the stream bottom. Schwertmann and Murad (1983) showed that ferrihydrite or freshly precipitated iron could be transformed to more stable phases (goethite and/or hematite) within approximately 210 days under pH 6.5-7 (the common pH level observed in Slate Creek). After remediation (such as capping) is implemented, reduced iron loadings and reduced precipitated iron depositions would be expected. Thus, it can be assumed that, without additional newly precipitated iron, the aging process of the existing iron sediment (from ferrihydrite to goethite/hematite) would continue.

In order to assess potential dissolution from aging sediment, stream travel time and proton-promoted iron dissolution kinetics and thermodynamics were investigated. Identifying travel time was necessary to consider the kinetic dissolution of iron. The estimated travel time for the mining-affected segment was slightly less than one hour under the modeled flow condition. For goethite/hematite, iron dissolution of 50 µg/L per hour (Brantley et al. 2008) or less than 10 µg/L with thermodynamics database under neutral pH solution was calculated. While ferrihydrite or freshly precipitated iron generated similar iron dissolution

(less than 10 µg/L) with the database, 110 µg/L per hour of iron could be generated with kinetics for ferridydrate dissolution (Jurjovec et al. 2004). The results indicate that the aging process would reduce the iron dissolution or would help to control the iron dissolution to be insignificant within the travel time, especially after 210 days when the all the pre-remediated iron would be transformed potentially to goethite/hematite.

In addition to the proton-promoted dissolution, potential iron reductive dissolution was evaluated under the remediated conditions. An organic matter degradation rate of 0.0007 (/h) (Dituro 2001) applied to background DOC concentration (3.3e-5 mol/L: estimated from in-stream DOC data) generated less than 10 µg/L per hour of iron. Thus, the contribution of iron from the reductive dissolution processes can also be considered negligible under the remediated condition.

Overall, Figure 4-3 below illustrates the simulated reduced iron condition.

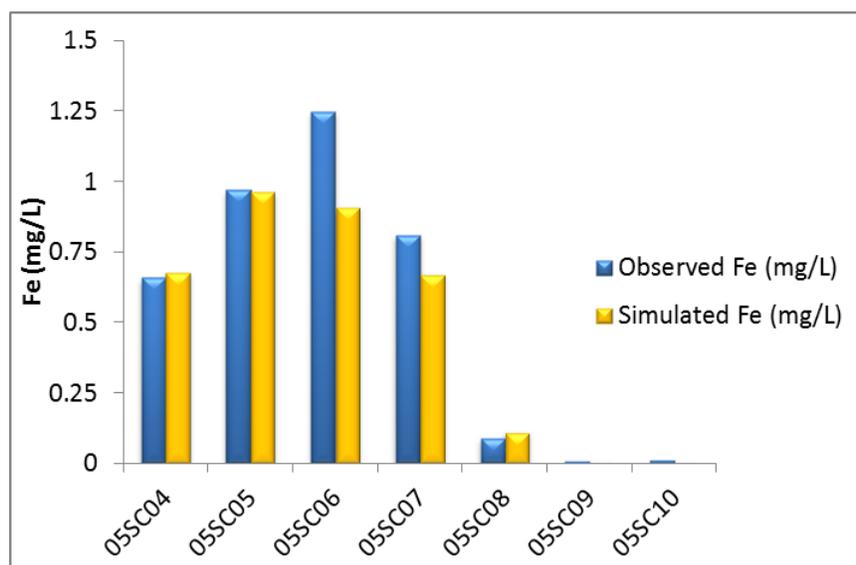


Figure 4-3. Model results for the reduced iron simulation.
(note: the TMDL numeric target is equal to 1 mg/L or 1,000 µg/L)

2. **Arsenic:** After iron was reduced to meet the criterion, a scenario to simulate arsenic reduction was conducted. Arsenic exceeded the drinking water criterion of 10 µg/L at stations 05SC05, 05SC06, and 05SC07. Due to the sediment contribution of arsenic to the water column, reductions to the iron sediment content as well as external arsenic sources resulted in meeting the drinking water criterion of 10 µg/L, as described below:
 - At stations 05SC05 and 05SC07, there were no major sources affecting the areas except for the existing sediment. Iron in sediment was reduced to control the sediment contribution of arsenic loadings. The sediment was reduced to 1.8% iron by weight, consistent with the freshwater sediment screening level (Table 2-3).
 - At station 05SC06, two reduction measures were taken. The first measure was to reduce iron sediment to the freshwater sediment screening level of 1.8% (Table 2-3) and the other management measure evaluated was to reduce the arsenic concentration in the tailings to 20 µg/L (from 47 µg/L of total arsenic).

Figure 4-4 below shows the results of the reduced total arsenic scenario, where arsenic concentrations are less than 10 µg/L. The background iron sediment concentration (iron sediment concentration from station 05SC01) was also examined with the selected external source reduction described above to evaluate the

effect on in-stream arsenic. The result confirmed that these reductions also achieved the arsenic criterion throughout Slate Creek.

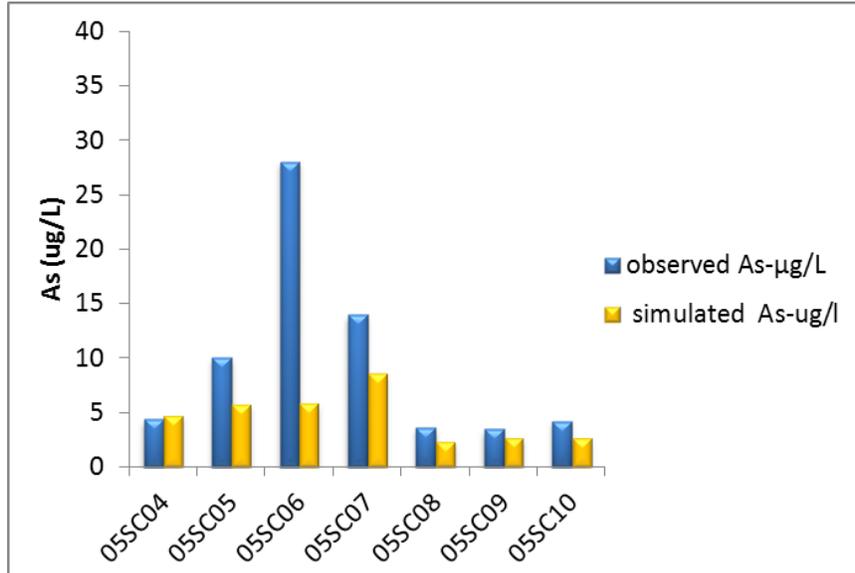


Figure 4-4. Model results for the reduced arsenic simulation.
 (note: the TMDL numeric target is equal to 10 $\mu\text{g/L}$)

- Antimony:** After arsenic was reduced to meet the criterion, antimony reductions scenarios were conducted. As antimony only shows weak affinity to the iron surface, direct reductions to all of the external source loading were required. All mining related sources (including the tributary, mine seep, and tailings) were reduced to 6 $\mu\text{g/L}$ for these scenarios. Figure 4-5 illustrates that this remediation scenario reduced total antimony to below 6 $\mu\text{g/L}$.

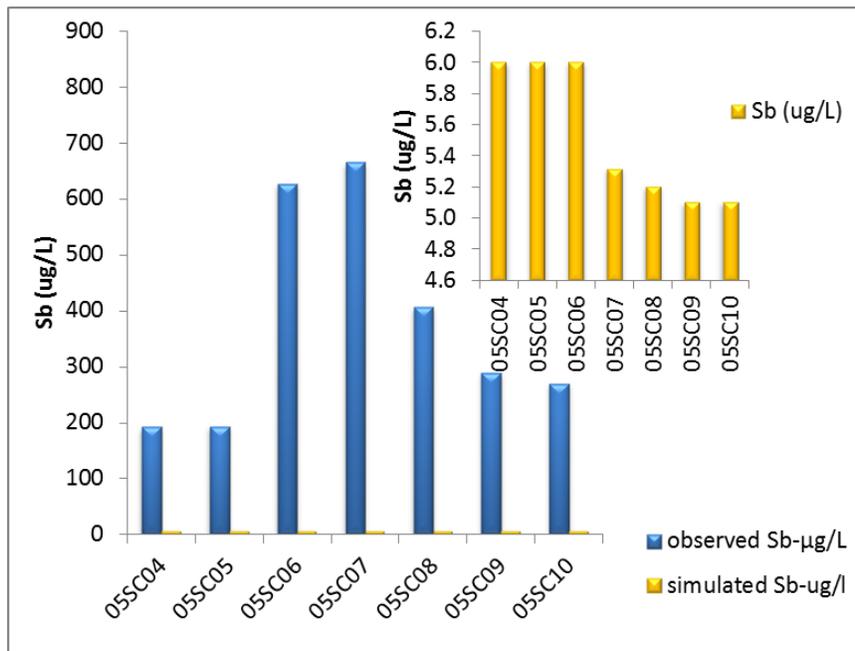


Figure 4-5. Model results for the reduced antimony simulation.
 (note: the TMDL numeric target is equal to 6 $\mu\text{g/L}$)

4.2.2. Application of Model Results

Results of the modeling process support several aspects of the TMDL analyses. They helped to inform the source assessment (Section 5), characterized conditions under which the creek sediment is a source of metals to the water column, identified reduction scenarios to meet TMDL numeric targets, and informed implementation alternatives and future monitoring recommendations (Section 7). Specifically, modeling results help to quantify and confirm the sources in Section 5 since the model incorporated all known sources, such as the tributary, mine seep, and other mining-related sources (Appendix A). They were also used to confirm the importance of sediment concentrations and internal cycling in Slate Creek and discussed how the different metals interact (Section 5.2.6). In addition, modeling scenarios were performed through an iterative process to evaluate attainment of the water quality criteria. These indicated that sediments were a source of arsenic to the water column and that a reduction in sediment iron percent is needed to attain arsenic water column criteria, while mining source reductions are needed to meet criteria for antimony. Sediment was not found to be a significant source of iron or antimony to the water column (Section 4.2.1). Overall, the model results were applied throughout the TMDL analyses and will be useful to guide future implementation.

5. Pollutant Sources

This section discusses the potential sources of antimony, arsenic, and iron to Slate Creek, including point, nonpoint, and natural sources. Alaska's 2012 section 303(d) list identified historic mining as the expected source (ADEC 2012a); however, other possible sources could include natural background sources and internal loading.

5.1. Point Sources

There are no current permitted point sources, including those under individual or general permits, discharging to Slate Creek. However, restoration activities in the future, if large enough in size, may require a construction general permit. Restoration activities are associated with implementation of these TMDLs to restore designated uses. Other development, such as park enhancement activities may include development of trails or campgrounds. These activities have the potential to disturb sediment (that may contain arsenic, antimony, and/or iron) and could result in increased metals loading to Slate Creek. Therefore, these sources are addressed in the TMDL with a future wasteload allocation.

5.2. Non Point Sources

All known current loadings to Slate Creek are associated with nonpoint sources. These sources are discussed below and receive load allocations in the TMDL.

5.2.1. Historic Mining

The former antimony mine located near the headwaters of Slate Creek is the expected primary source of antimony, arsenic, and iron loading. This antimony deposit occurs as stibnite (Sb_2S_3) quartz veins in the Birch Creek Schist and the Slate Creek Mine produced approximately 700 tons of antimony ore between 1916 and 1983 (Brabets and Ourso 2013). Pyrite (FeS_2) and arsenopyrite (FeAsS) are commonly associated with stibnite and are the origins of arsenic and iron in the watershed. Historic mining activities removed natural topsoil and left exposed mineral-laden substrate as well as mining waste (tailings and a settling pond and trench) and eroding stream banks. These practices resulted in contamination of the creek water as well as deposition of sediment in the creek bottom that is contaminated with metals. NPS restoration efforts began in 1997 to improve drainage from four acres of disturbed upland and stream channel areas near the exposed ore body and continued through 2010 with additional removal of mine tailings (USEPA 2013); however, recent data continue to show antimony, arsenic, and iron contamination. Figure 5-1 displays Slate Creek in June 2010 prior to reclamation efforts on the left panel and after reclamation efforts in September of 2010 on the right panel. The rerouting of the stream around the former mine pit is illustrated in these images.

High concentrations of antimony, arsenic, and iron have been measured in surface water at the USGS monitoring location (just downstream of the historic mine and tailings). Specifically, in 12 samples from 2008-2011, the antimony concentrations were 14 to 60 times greater than the antimony drinking water criterion. For arsenic, six samples collected from 2008-2009 were below the associated criterion; however, the subsequent samples in 2010 and 2011 were two to seven times above the arsenic drinking water criterion (Brabets and Ourso 2013). Concentrations of dissolved iron were greater than 1,000 $\mu\text{g}/\text{L}$ in 10 out of the 12 samples (Brabets and Ourso 2013). Streambed sediment was also sampled by USGS in 2008 and both antimony and arsenic concentrations were over two orders of magnitude above sediment quality guidelines (Buchman 2008; Table 2-3). Spatially distributed data from Ritchie et al. (2013) also confirm these findings (note: neither dataset reported iron in the sediment as a percentage, so the data could not be compared to the sediment quality guidelines). Antimony, arsenic, and iron concentrations in water and sediment from the mine waste seep station (05SC02 and 07SC03 in Figure 3-3) as well as other stations near and downstream of the former mine and tailings exceeded applicable criteria and guidelines (Ritchie et al. 2013).

Contaminated groundwater from the restored former mining site could be contributing to the antimony, arsenic, and iron impairments in Slate Creek. In addition, runoff over the restored site is likely contributing antimony,

arsenic, and iron loads when in contact with contaminated sediment that is still present (Section 4). Despite the restoration performed to date, without additional management the concentrations of antimony, arsenic, and iron are expected to remain elevated in Slate Creek.



Figure 5-1. Conditions before (June 1, 2010: left) and after (September 2010: right) reclamation at Slate Creek; Photos from Tim Brabets, USGS, and Denali National Park and Preserve (Source: Brabets and Ourso 2013)

5.2.2. Potential Park Enhancement and Restoration Activities

As discussed in point sources above, future restoration or park enhancement activities have the potential to disturb sediment (that may contain arsenic, antimony, and/or iron) and could result in increased metals loading to Slate Creek. If future restoration or park enhancement activities are small enough in size that they do not require a construction general permit, they are still addressed by these TMDLs as a nonpoint source.

5.2.3. External Nonpoint Sources

According to the data reviewed, recent monitoring supports the assumption that stormwater sources do not seem to be a significant contributor of antimony, arsenic, and iron to Slate Creek. There are no specific sources of these metals except those associated with historic mining activities (including internal loading and a minor tributary located in close proximity to the mine site) and concentrations in water were low upstream of the mine (station 05SC01 in Figure 3-3). Water concentrations moving downstream do not increase significantly (although internal cycling of the metals, as described below and in Section 4, does impact the water concentrations), which would be expected if runoff was a source to Slate Creek.

5.2.4. Natural Sources

According to the Ritchie et al. (2013) data reviewed, recent monitoring of background water antimony, arsenic, and iron concentrations upstream of the mine (station 05SC01 in Figure 3-3) supports the assumption that natural sources are not significant contributors of antimony, arsenic, and iron load to Slate Creek in the water column. While the water concentrations are low, background sediment concentrations for antimony and arsenic are higher than sediment quality guidelines (968 mg/kg antimony and 1,900 mg/kg arsenic at 05SC01 [Figure 3-3]; iron sediment data were not presented as a percentage) (Ritchie et al. 2013). Since the data suggest that background sediment concentrations are high, natural background should continue to be considered as a potential source and evaluated through further monitoring.

5.2.5. Tributary Inputs

A minor, unnamed tributary enters Slate Creek near the historic mine site (05SC03 in Figure 3-3). Water concentrations at this location are higher than the drinking water criteria for both antimony and arsenic and sampling of iron in 2005 was higher than the chronic aquatic life criteria. Concentrations in this tributary water

were generally similar to concentrations found downstream of the mine. Sediment concentrations at the tributary station were lower than stations near and downstream of the historic mine; however, they still exceeded the sediment quality guidelines by ~two orders of magnitude (Ritchie et al. 2013). The data indicate that tributary concentrations of water and sediment exceeded associated criteria and guidelines; therefore, tributary inputs are a potential source of pollutant loading to Slate Creek, although the loading is expected to be intermittent and associated with very low flow.

The model assumed that 10 percent of flow to 05SC04 is associated with the minor tributary based on field observations, meaning the tributary flow was estimated at 0.046 cfs in August 2005 (Appendix A). Though concentrations of arsenic, antimony, and iron were high in the tributary samples from 2005, this was a minor source of total metal loads to the mainstem of Slate Creek due to the low level of flow assumed to come from this tributary (Appendix A).

5.2.6. Internal Loading

Recycling of antimony, arsenic, and iron is expected as the sediment and water interface in Slate Creek. Metals in the water column may precipitate out as co-precipitated and/or adsorbed phases over time, but some of this sediment-associated load may go through chemical reduction and dissolve back into the water column (thereby increasing the water column concentration), especially due to changes in pH, redox conditions, and potential temperature shifts.

Sediment concentrations throughout the study area are several orders of magnitude above the sediment quality guidelines. Ritchie et al. (2013) found that iron plays a key role in controlling the transport of the trace elements. Iron oxide present in Slate Creek deposits as flocs and coatings on minerals (e.g., clay-sized minerals) when the low-pH mine drainage mixes with runoff from the non-mined area, resulting in increased pH values in this combined drainage. Adsorbed arsenic may settle out of the water column with these iron oxide flocs, but some of this load may go through chemical reduction and dissolve back into the water column. Antimony can also be subject to this process; however, it has a lower affinity for partitioning to mineral surfaces, which results in farther downstream transport (Ritchie et al. 2013). Overall, sorption to iron compounds is an important sink (which will decrease water column and increase sediment concentrations through precipitation to the sediment) and potential source (through chemical reduction of the sediment-associated pollutant, which will increase water column and decrease sediment concentrations) for antimony, arsenic, and iron in Slate Creek.

The modeling study (Section 4) focused on whether sediments are a source of the high metal concentrations in the stream. The model was used to quantify acceptable levels of antimony, arsenic, and iron in the water and sediment to meet TMDL numeric targets for Slate Creek. The model results were used to confirm the importance of sediment concentrations and internal cycling in Slate Creek, which subsequently informed the allocations and implementation recommendations (see Sections 6 and 7). The modeling results found that sediments were a source of arsenic to the water column and that a reduction in sediment iron percent is needed to attain arsenic water column criteria. Sediment was not found to be a significant source of iron or antimony to the water column (Section 4).

6. TMDL Allocation Analysis

A TMDL represents the total amount of a pollutant that can be assimilated by a receiving waterbody while still achieving water quality standards—also called the *loading capacity*. In TMDL development, allowable loadings from all pollutant sources that cumulatively amount to no more than the TMDL's loading capacity must be established and thereby provide the basis for establishing water quality-based controls.

A TMDL for a given pollutant and waterbody is composed of the sum of individual waste load allocations (WLAs) for point sources and load allocations (LAs) for nonpoint sources and natural background loads. In addition, the TMDL must include a margin of safety (MOS), either implicitly or explicitly, that accounts for the uncertainty in the relationship between pollutant loads and the quality of the receiving waterbody as well as an allocation for future sources (if determined necessary). Conceptually, this definition is denoted by the equation

$$\text{TMDL} = \Sigma \text{WLAs} + \Sigma \text{LAs} + \text{MOS} + \text{Future Allocation}$$

The analytical approach used to estimate the loading capacity and allocations for Slate Creek is based on the best available information to represent the impairments and expected sources.

6.1. Loading Capacity

The loading capacity is equivalent to the TMDL and is the greatest amount of a given pollutant that a waterbody can receive without exceeding the applicable water quality standards, as represented by the TMDL numeric target. Almost all antimony, arsenic, and iron loads entering Slate Creek are by runoff pathways associated with the historic mine. Recent modeling analyses also indicate that internal loadings impact the water column concentrations.

The TMDL expresses the loading capacity for antimony, arsenic, and iron in Slate Creek as concentrations, equivalent to Alaska's numeric drinking water quality criteria of 6 µg/L antimony and 10 µg/L arsenic and the chronic aquatic life criteria of 1,000 µg/L iron. These targets are protective of all freshwater designated uses¹. A concentration-based TMDL is directly comparable to the applicable water quality criteria and as such, is easily communicated.

A concentration-based TMDL is appropriate because using a more complicated analysis to estimate antimony, arsenic, and iron loads from mine tailings would require additional data collection and would not provide additional guidance or benefit to the subsequent planning and implementation actions.

Conceptually, the loading capacity represents the sum of WLAs, LAs, and MOS. Therefore, when the loading capacity is expressed as a load, it is divided among WLAs for point sources and LAs for nonpoint sources, minus a MOS. In those cases, the allowable load is a finite mass of pollutant that can be divided into individual loads for each source, that when combined represent the total loading capacity. However, when the loading capacity is expressed as a concentration, this additive approach is not applicable. As a concentration, the loading capacity represents an allowable ratio of the pollutant to water. Therefore, if the loading capacity is expressed as a concentration in Slate Creek, all allocations are equivalent to, rather than a portion of, the loading capacity. In other words, the target concentration implicitly represents an acceptable (but undefined) loading rate.

Necessary reductions in existing concentrations were calculated for Slate Creek to identify the reductions needed to meet the loading capacity and corresponding water quality standards. Reductions were calculated based on the

¹ TMDLs are typically based on *loads* of pollutants—some allowable mass of a pollutant over a specified time period such as kilograms per day. The loading capacity is then divided among WLAs for point sources and LAs for nonpoint sources, minus a MOS.

maximum observed antimony, arsenic, and iron concentrations (subsequent to the recent site improvements in 2010) relative to their respective load capacity (that is equal to the applicable water quality criterion):

$$\text{Percent Reduction} = \frac{(\text{Maximum Measured Concentration} - \text{Load Capacity})}{(\text{Maximum Measured Concentration})} \times 100$$

Table 6-1 summarizes the antimony, arsenic, and iron TMDLs for Slate Creek.

Table 6-1. TMDL allocation summary for antimony, arsenic and iron in the water column

Parameter	Loading Capacity (µg/L)	Future WLA (µg/L)	LA (µg/L)	Margin of Safety	Future Growth	Maximum Observed after August 2010 (µg/L)	Percent Reduction to Meet LA (%)
Antimony	6	6	6	Implicit	N/A	158 ^a	96%
Arsenic	10	10	10	Implicit	N/A	69.9 ^a	86%
Iron, dissolved	1,000	1,000	1,000	Implicit	N/A	2,980	66%

N/A = not applicable

^a Data for 2011 from Brabets and Ourso (2013) are filtered, not total; included as a conservative assumption for the implicit MOS.

Internal modeling of the Slate Creek system showed that in order to meet arsenic water column criteria, a reduction in iron in the sediment is required. Sediment levels of iron need to be reduced to the background level of 1.8% iron to meet the arsenic numeric target (and concentration-based loading capacity) throughout the system.

Table 6-1 summarizes the water column WLAs and LAs for Slate Creek along with the necessary percent reductions of antimony, arsenic, and iron concentrations from the maximum observed antimony, arsenic, and iron concentration in Slate Creek following 2010 remediation activities while considering an implicit margin of safety (note: the maximum observed concentrations represent the worst case scenario). The reductions in existing concentrations are provided to illustrate the relative magnitude of impairment and associated reductions needed to meet the loading capacity and TMDL numeric targets. Using the highest observed concentration to calculate reductions reflects the worst case scenario. Therefore, the reductions represent the levels needed to ensure that water quality criteria are met during all conditions.

6.2. Wasteload Allocation

There are currently no known active permitted discharges of antimony, arsenic, and iron to Slate Creek. However, additional construction in the watershed is anticipated associated with restoration activities that will facilitate implementation of these TMDLs as well as potential park enhancement projects (Section 5). At least some of these construction activities are expected to be permitted by an APDES construction general permit and disturb sediment; therefore, they are a potential source of antimony, arsenic, and iron to Slate Creek. Therefore, metals loads delivered to Slate Creek from the potential construction permits are addressed through the future WLA component of these TMDLs. The concentration-based WLAs are equal to the loading capacities for antimony, arsenic, and iron (Table 6-1).

6.3. Load Allocation

The LA is the portion of the loading capacity allocated to nonpoint source discharges to the waterbody. Nonpoint sources are typically represented by loads carried to receiving waters through surface runoff resulting from precipitation events.

As discussed in Section 5, runoff from historic mining is the primary source of antimony, arsenic, and iron to Slate Creek. Other potential sources include natural background, tributary inputs, and internal cycling. The concentration-based LAs are equal to the loading capacities for antimony, arsenic, and iron (Table 6-1).

6.4. Margin of Safety

The MOS accounts for any uncertainty concerning the relationship between pollutant loading and receiving water quality. The MOS can be implicit (e.g., incorporated into the TMDL analysis through conservative assumptions) or explicit (e.g., expressed in the TMDL as a portion of the loading) or a combination of both. An implicit MOS was included in this TMDL document.

Meeting the Alaska water quality criteria for antimony, arsenic, and iron results in the inclusion of an implicit margin of safety. Determination of an explicit margin of safety is not necessary for this particular TMDL because in presenting the allocations as a concentration at the water quality criteria for antimony, arsenic, and iron, the sources will comply with the water quality standards and there will be no uncertainty involved.

In addition to the use of water quality criteria for the loading capacity, other conservative assumptions were included that contribute to the implicit MOS. These assumptions include the determination of existing concentrations and assumptions made during the internal loading modeling. Specifically, by using the maximum (as opposed to average or median) observed antimony, arsenic, and iron concentrations in Slate Creek to represent existing conditions, the necessary reductions reflect the worst case scenario. In addition, for antimony and arsenic, the maximum observed values used to represent existing conditions were filtered measurements, not total (total results are directly comparable to the water quality criteria), resulting in an additional conservative assumption regarding required reductions.

6.5. Seasonal Variation and Critical Conditions

Seasonal variation and critical conditions associated with pollutant loadings, waterbody response, and impairment conditions can affect the development and expression of a TMDL. Therefore, TMDLs must be developed with consideration of seasonal variation and critical conditions to ensure the waterbody will maintain water quality standards under all expected conditions.

For Slate Creek, the times of highest loading and worst impairment are expected to be during the summer months when the highest temperatures occur. Higher temperatures decrease the solubility of oxygen in water, promote bacterial activity (bacteria production increases CO₂ and decreases pH, which affect the balance of pollutants between the water and sediment), and lead to more reducing conditions. These conditions would decrease the antimony, arsenic, and iron load that oxidizes and precipitates from the water column to the sediment, thus increasing the dissolved fraction in the water column.

It is important to note that applicable water quality criteria for antimony, arsenic, and iron apply year round and impairment has been observed throughout the spring and summer monitoring periods. No known data are available during the winter months. Historically, data have only been collected during the spring, summer, and fall months, and the extent to which impairments occur during the winter is unknown.

In summary, available data on antimony, arsenic, and iron as well as aquatic life suggest that spring through the fall months reflect the critical period. However, conditions during the winter months have not been assessed, and loading reductions should be pursued year-round to address impairments. The concentration-based TMDL approach is believed to meet water quality criteria during the unmonitored winter months.

6.6. Reasonable Assurance

USEPA requires that there is reasonable assurance that TMDLs can be implemented when the TMDL is a mixed source TMDL (USEPA 1991). A mixed source TMDL is a TMDL developed for waters that are impaired by both point and nonpoint sources. The WLA in a mixed source TMDL is based on the assumption that nonpoint source load reductions will occur. Reasonable assurance is necessary to determine that a TMDL's WLAs and LAs, in combination, are established at levels that provide a high degree of confidence that the goals outlined in the TMDL can be achieved. This TMDL is not currently a mixed source TMDL since there is no construction general permit in place; however, since there is expected to be a construction general permit in place to address future restoration and park enhancement activities (which will receive a WLA), reasonable assurance has been included.

The technical approach applied for these TMDLs characterizes the contribution of metals to Slate Creek from both nonpoint sources and future point sources. The future WLA for Slate Creek was allocated for the potential construction general permit, but is also addressed by the nonpoint source loading capacity if the projects do not require permits. All allocations are set equal to the concentration-based loading capacity.

Restoration activities, monitoring, technical and financial assistance, permit administration, and permit enforcement will all be used to ensure that the goals of this TMDL are met. The following rationale helps provide reasonable assurance that the Slate Creek TMDL goals will be met.

- **The Alaska Storm Water Guide:** The diversity of Alaska's geography, geology and climate can make designing and implementing stormwater controls particularly challenging. The *Alaska Storm Water Guide* (ADEC 2011) provides detailed guidance on the implementation of stormwater BMPs, including those associated with construction activities, to comply with water quality standards of receiving waters. *Alaska Storm Water Guide* addresses some of the unique challenges posed by the diversity of Alaska's climate, soils, and terrain and makes recommendations about the design and selection of stormwater BMPs in an effort to optimize their effectiveness. Chapter 2 of *Alaska Storm Water Guide* provides stormwater considerations for the various climatic regions in Alaska (Slate Creek is in the interior region).
- **Identified commitment to achieve the nonpoint source reductions:** With regard to LAs for nonpoint sources, programs including Section 319 funding are available. Section 7 provides more detail on implementation opportunities for the Slate Creek watershed. NPS has already expressed support for this TMDL, which adds to the assurance that metals in the Slate Creek watershed will meet the concentration-based load allocations and attain water quality standards. This assumes that the activities described below are implemented and maintained.
 - In a 2010 fact sheet, NPS indicated that Denali staff are working with partners to determine if restoration work has improved water quality. Specifically, "a true measure of mining restoration success will be when ... Slate Creek ... can be taken off of the list because they meet water quality standards" (Denali National Park and Preserve 2010). Similarly, a 2010 article described the restoration efforts on Slate Creek to repair previous mining damage, and stated that the improvements to the system offer a promising future for the watershed and continued water quality monitoring will determine if water quality has improved (Adema et al. 2010).
 - In addition, a commitment to restore mined areas is reiterated in a recent reclamation plan from NPS and USGS for Stampede Creek, which has similar impairments to Slate Creek. Specifically, the plan indicates that abandoned mines and reclamation efforts are listed as 'High Priority' for DENA (Mangi Environmental Group 2005; Karle 2007) and well-planned and comprehensive reclamation efforts are needed to clean-up former mining claims where substantial environmental disturbance has occurred.
- **Monitoring and Tracking Approach to Evaluate Progress:** The implementation section below includes a description of monitoring recommendations to evaluate progress and make adjustments, if necessary.

- **Follow-Up Actions:** ADEC has the legal authorities that would allow the possibility of requiring more stringent permit limits or more effective nonpoint controls if there is insufficient progress in the expected nonpoint source control implementation. While ADEC is authorized under Alaska Statutes Chapter 46.03 to impose strict requirements or issue enforcement actions to achieve compliance with state water quality standards, it is the goal of all participants in the Slate Creek TMDL process to achieve clean water through cooperative efforts.

To provide additional assurance beyond existing programs and planned activities, the actions described in the Implementation Section (Section 7) are provided to better understand how to implement the WLA and LA in the TMDL. The implementation section of this TMDL describes management activities that can be used to achieve these actions.

6.7. Future Growth

No allocation is provided for future growth because the entire drainage area is within Denali National Park and Preserve. Mining is prohibited in the park as per the Mining in the Parks Act of 1976. In addition, this area has no road access; therefore, no additional development is expected to occur.

6.8. Daily Load

A TMDL is required to be expressed as a daily load; the amount of a pollutant the waterbody can assimilate during a daily time increment and meet water quality standards. The TMDLs for antimony, arsenic, and iron are presented as maximum concentrations allowed in the water column. The allowable concentrations are applicable at all times and can therefore be applied on a daily basis.

7. Implementation and Monitoring Recommendations

To date, the NPS has reconstructed a portion of the Slate Creek floodplain and created a drain to intercept groundwater flow from a small open mining pit. The NPS moved an erosion-prone tailings pile away from the floodplain and installed erosion control materials. The project seeded, limed, and fertilized remaining tailings piles to establish vegetative cover and prevent further erosion. The project also moved a 400-foot portion of the stream away from an area that contained the pit mines in August of 2010.

The year of data collected post-restoration (2011) continued to show considerable exceedances of water quality criteria (note: reductions required were based on the maximum concentration observed for each pollutant after August 2010; Section 6.1). Additional management measures are likely necessary to meet designated uses and monitoring is crucial to refine sources and measure progress. This section of the report presents recommendations for additional implementation and monitoring to assist in meeting the antimony, arsenic, and iron TMDLs for Slate Creek.

7.1. Implementation

Implementation activities in the Slate Creek watershed are subject to considerable challenges, including the remote location with difficult access, expensive management measures, and a sensitive environment (Adema et al. 2010; Environmental Compliance Consultants, Inc. et al. no date). Specifically, implementation activities can improve water quality conditions in Slate Creek; however, the practicality of the activities is a concern as removal of contaminated material is not practical. Therefore, it is important to consider options to target management measures on the pertinent sources. The bulleted list below identifies some of these options.

- **Detailed Source Assessment:** A detailed monitoring study would be beneficial to focus implementation activities on the most critical source pathways. Monitoring should specifically focus on quantifying the surface and groundwater loads associated with antimony, arsenic, and iron, and should include periods of higher flow to fully characterize surface water contributions. Isolating either surface or groundwater sources will help focus implementation activities on the pertinent pathway, thereby efficiently spending resources (although, data could indicate both pathways require management).
- **Designated Use Study:** Water quality standards associated with Slate Creek protect the drinking water designated use. Because of the remote location of the Slate Creek watershed within a national park, it is unlikely that this drainage will be used as a drinking water source. Aquatic life designated uses may be more applicable. Therefore, a use attainability analysis may be useful to accurately identify the designated uses for the Slate Creek watershed. If the water quality criteria were adjusted, the required reductions would be lower, which may lead to selection of different (and potentially less expensive) management measures. However, it should be noted that if this type of analysis identified different water quality criteria, the TMDL would need to be modified; therefore, the cost and time associated with revising the TMDL should be considered during study planning and implementation.
- **Traditional Management Measures for Mined Sites:** There are several management measures that are traditionally used for restoration of mined sites. The first traditional activity includes the removal of the mining-related material (potentially including material dredged from the creek itself) and placing this material in a repository designed to contain the contamination. This option is likely impractical for the Slate Creek watershed due to the remote location and difficult access. Other traditional activities focus on the critical pathway (s). To prevent surface runoff, mine tailings and related material are capped in place. To prevent seepage into a creek associated with interflow or groundwater, impermeable barriers are used to line the stream. Performing both of these actions would address both surface and groundwater pathways; however, a detailed source assessment (as described above) could identify the more crucial pathway.

The subsections below present pollutant-specific management measures that are expected to result in attainment of designated uses. These measures may not be the most efficient, but without further study they are likely the most direct path to meeting the TMDL.

7.1.1. Iron

To meet water quality criteria for iron, one implementation option would be to create conditions in which iron is precipitated out in insoluble form. This could be achieved through aggressive calcite addition that helps to reduce iron concentrations in the water and keeps low reduction potential at the sediment surface (Section 4). Based on the modeling analyses, 83 pounds per day of calcite is the dosage required to reduce iron concentrations in water. This effort alone is expected to reduce iron to meet the TMDL numeric target.

If implementation strategies, such as capping and lining described above, successfully disconnect the hydrologic connectivity of mining sources, the pre-remediated high iron solution would be replaced with background solution within approximately 150 days. Thus, 150 days of calcite dosing should provide enough alkalinity while the natural attenuation processes (flushing out and aging) advances after implementation of management measures. If continuous alkaline dosing is not feasible, implementing a calcite or magnesite barrier in the aquifer could provide similar results (9 kg/m² or 1.9 pound/feet² of calcite barrier could adequately provide the necessary alkaline dosage for 150 days). These calculations were based on estimated diffuse source flow around the stream length affected by mining sources (stations 05SC04, 05SC05, and 05SC06), estimated wetted perimeter length along the segment where diffuse flow is assumed to converge, and the alkaline dosage derived during modeling (Section 4.2.1). While this activity will reduce iron in the water column, it does raise iron concentrations in the sediment, which can influence arsenic concentrations (see discussion for arsenic below).

7.1.2. Arsenic

The TMDL analyses assumed that iron concentrations in the water column were reduced to meet the water quality criterion before arsenic was evaluated. This is because arsenic has a strong affinity for iron, so any changes in iron concentrations will affect arsenic concentrations. Based on the model scenarios (Section 4), the water quality TMDL for arsenic cannot be met through reductions in the inflow alone and steps will need to be taken to reduce iron in the sediment as well as in the water column (if the activities mentioned above for iron are addressed first, the resulting iron concentrations in the water column will be reduced to the water quality criterion). Iron would have to be removed from the bottom of Slate Creek to attain 1.8% iron content (Table 2-3) or background sediment iron concentrations represented by station 05SC01 (Ritchie et al. 2013). This can be achieved through dredging of stream bottom material near the tailing piles and downstream to station 05SC07; thereby, creating a problem regarding what to do with the removed sediment. Removal of the material outside of the watershed is impractical because of the remote location and limited access. Moving the material to another location in the watershed and subsequently following recommendations associated with the ‘Traditional Management Measures for Mined Sites’ above regarding capping and lining may be an alternative. In addition to the iron reductions, arsenic concentrations from the tailings should be reduced to 20 µg/L (down from 47 µg/L of total arsenic). Depending on whether this source is associated with a surface or groundwater pathway, capping or lining could help achieve these reductions (see ‘Traditional Management Measures for Mined Sites’ above). Overall, the modeling results predict that reducing sediment iron concentrations and reducing arsenic concentrations in the inflow from the tailings will result in meeting the arsenic water column targets.

7.1.3. Antimony

Attainment of the antimony TMDL focuses on reductions to external sources as antimony only shows a weak affinity to iron. Specifically, all mining related sources (including the tributary, mine seep, and tailings) would need to be reduced to 6 µg/L to result in attainment of the antimony numeric target throughout Slate Creek. A detailed source assessment, as described above, would be useful to identify whether the specific mining-related sources (tributary, mine seep, and tailings) reach the creek through surface water, groundwater, or both. The pathway influences the necessary management measure to reduce antimony concentrations. As mentioned above,

capping the source material would reduce surface runoff, while lining the creek is expected to reduce inputs from contaminated groundwater.

7.2. Monitoring Recommendations

The internal loading simulation conducted for this TMDL effort (see Section 4) presents results that can be used to inform future implementation and monitoring for Slate Creek. While the model results show that reducing the Slate Creek bottom sediments to 1.8% iron by weight (Table 3-1) and increased levels of calcite in the water column could facilitate the reduction of metals in the water column, it should be noted that there is much uncertainty surrounding the internal loading model due to limited data. The amount of available data to use as input to the PHREEQC model was limited, which resulted in the use of assumptions, estimates, and literature values rather than site-specific data. This can lead to uncertainty in the results.

Additional monitoring could support future model development using site-specific data to more accurately represent Slate Creek. Specifically, in addition to the list of the parameters already collected in and around the creek, additional flow and instream and sediment chemistry data would be helpful. These additional data would provide more confidence in evaluating the site conditions, the fate of the leachate from mine sites, and the resulting water column and sediment conditions.

The following monitoring activities are recommended to support additional source assessment analyses (through the use of a chemical model):

- Monitor flow or perform a dye study to evaluate the flow mass balance throughout Slate Creek to characterize the detailed hydraulics and hydrology of drainage.
- Measure major cations and anions, antimony, arsenic, and iron concentrations in groundwater, surface water, sediment throughout different periods, especially in the mining affected area and nearby reach segments.
- Collect groundwater background concentrations of antimony, arsenic, and iron to compare to previous background concentration estimates from historic data.
- Collect additional spatial water column, sediment, groundwater, and mine waste tailing leachate (subsurface) data to support model refinement using site-specific data including: total organic carbon/dissolved organic carbon, total inorganic carbon, alkalinity, calcium, magnesium, sodium, ammonium, sulfate, chloride, cation exchange capacity (creek bottom sediment), and sediment antimony, arsenic, and iron concentrations from creek sediments using sequential extraction method to identify different metal conditions (exchangeable, carbonate, oxides, etc.).

These data would provide additional detail to refine the chemical model. A more detailed model could be used to support more specific model scenarios, thereby identifying more targeted management measures. In addition, data for metals and related parameters (identified in the last bullet above) associated with specific sources or pathways can also be used to measure progress; however, Slate Creek water quality data are necessary to measure attainment of water quality standards. Specifically, long-term collection of surface water quality data in Slate Creek (at multiple locations along the creek) for antimony, arsenic, and iron can be used to measure progress and quantify success of the implementation activities.

8. Public Comments

The notice for the public review period was posted on [Date], and the review period closed on [Date]. The notice was posted in the local newspaper [name of newspaper], on DEC's website, and on the State of Alaska's Public Notice Web Site. A fact sheet was also available on DEC's website.

Comments on the TMDLs were received from XXXX. Comments and additional information submitted during this public comment period were used to inform or revise this TMDL document. See Appendix B for detailed information on the response to comments.

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Appendix A

Supplemental Analysis of Water and Sediment Quality: Modeling Details

The USGS's pH-Redox-Equilibrium-Equations in C and C++ Model (PHREEQC model; Parkhurst and Appelo 2013) was selected to evaluate iron, arsenic and antimony's fate and transport in Slate Creek and to support TMDL analyses. PHREEQC is a computer program used to simulate chemical reactions and transport processes in a waterbody. The model is derived from the Fortran program PHREEQE (Parkhurst et al. 1980) and is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces, but also includes the capability to model kinetic reactions and transport reactions. Considering the potential sediment contribution of antimony, arsenic, and iron between the sediment and water interface, the reactions and functionalities included in the model are appropriate for this modeling study. The modeling output reflects the various metals sources, including the mining-affected area, tailing piles, and the potential effects from the upstream sediments. This appendix describes the data used for the modeling study, model configuration, key processes, and model results. Load reduction scenarios and application of the model results in the TMDL are described in Section 4 of the TMDL report.

Data Availability

Three sets of data were available and potentially useful for this modeling analysis: Brabets and Ourso (2013); Eppinger et al. (2000); and Ritchie et al. (2013). USGS data were collected from June 2008 through September 2011 (Brabets and Ourso 2013). Eppinger data were collected in August 1998 (Eppinger et al. 2000) and the Ritchie et al. (2013) data were collected in August 2005 and 2007 (Section 3.1).

The 2005 Ritchie et al. data (2013) were selected for modeling based on the synoptic nature of the longitudinal data set collected from both the water column and the sediments on the same date. These data also reflect the known sources to Slate Creek (Figure 3-3; Ritchie et al. 2013). The data collected in 2007 provided similar information; however, there were fewer sampling locations and no sediments data were collected. The USGS and Eppinger data did not provide spatially-distributed data, which were critical for model development and understanding the system. Although these data were not used directly for modeling, they were considered and applied to support model configuration and assumptions made during model simulations (Brabets and Ourso 2013; Eppinger et al. 2000).

Configuration of the Reactive Transport Model

Model configuration requires representation of system hydraulics and water quality. These will ensure that system hydrology and pollutant loading are characterized as accurately as possible using the available data and information. This section describes the configuration of the Slate Creek PHREEQC model, including the hydraulic configuration and inputs as well as the boundary conditions used to characterize other inputs to the system (note: boundary conditions are used to represent any exchange of water into or out of the model network).

Hydraulic Configuration and Inputs

The Slate Creek model was configured to represent eight model segments. The segmented locations were based on the available water quality data along Slate Creek. Figure A-1 shows the water quality sampling locations (e.g., 05SC01; see Figure 3-3 for a map with these locations) with the identified external sources and the river meter associated with the model segment in parentheses.

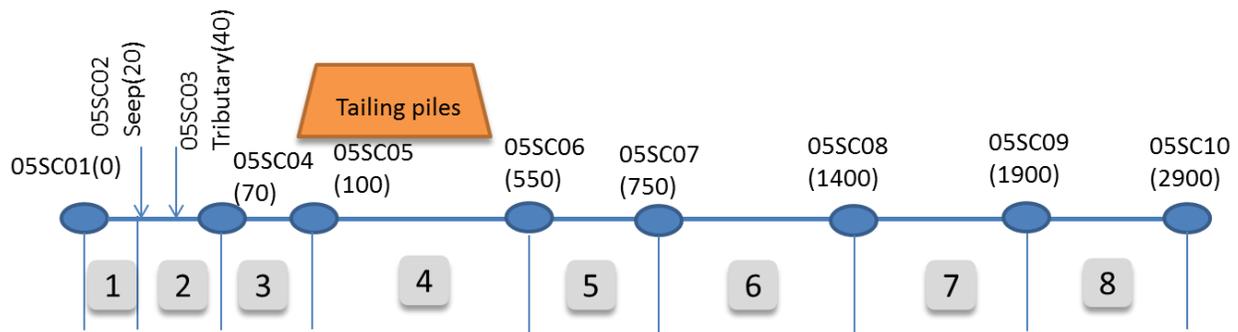


Figure A-1. Slate Creek model segments.

The transport mechanisms in Slate Creek were assumed to be dominated by advection processes simulated by a plug flow-mixing model. This type of model is used to represent chemical reactions in a continuous, flowing system, where fluid is simulated as passing (or flowing) through a series of “plugs” that are well-mixed and uniform in their composition. Specifically, each channel segment (i.e., plug) was assumed to be well-mixed and the simulated solutes were shifted to the next downstream segment (i.e., the flow between segments or plugs) after all considered reactions were applied and simulated (resulting in the well-mixed plug). Figure A-2 illustrates a conceptual model of the interactions between and within the modeled segments as part of the plug-flow mixing model. Specifically, the sediment and the water interactions are shown by the red arrows (within the segment or plug) and the transport mixing mechanisms with reactions are represented by the blue arrows (flowing from one plug to the next) (Figure A-2).

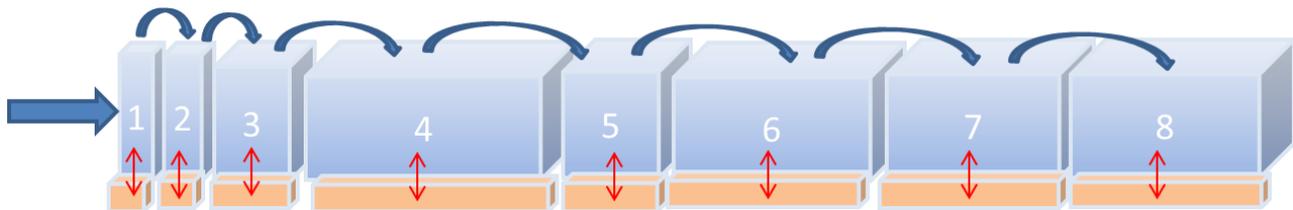


Figure A-2. Conceptual model of interactions between and within modeled segments.

In order to simulate the fate and transport of metals in Slate Creek, it was important to understand the spatial distribution of external sources as well as the potential metal contribution from the sediment to the water column (or vice versa). To quantify external source contributions, flow information associated with each source is critical as flow determines the transport pathways and metal loads into the main stem of the creek. There were no available flow measurements from the Ritchie et al. (2013) data, but stream depths (2005 and 2007) and widths (2007) were available. In addition, Brabets and Ourso provided one record of the hydrogeometry of the creek at their sampling location (USGS 15547575), including width (4.5 feet), average velocity (1.3 feet per second [ft/s]), and flow (1.5 cfs) (2013).

Without additional field data related to flow parameters, an alternative approach was developed to estimate flow for the model. Specifically, the Manning equation was applied to calculate stream flow and velocity using the available data and additional physical information of Slate Creek. Flow and velocity for each model segment were estimated through the following steps:

1. Initially, the slope of each segment was estimated using a topographic map and Google Earth (<http://www.google.com/earth/>).
2. The general stream cross-section was assumed to be a trapezoidal shape with a side slope of 1:1. The limited field pictures from the Ritchie et al. (2013) and Brabets and Ourso (2013) support this assumption regarding the general shape.

3. Measured stream depths and widths (Ritchie et al. 2013) were used to estimate the stream bottom length in conjunction with the trapezoidal assumption.
4. Once quantification of the stream geometry was complete, the Manning equation was applied to derive the estimated flow and velocity using an initial Manning's n of 0.04, which is within range for winding streams with some stones and weeds (Chow 1959).
5. The estimated flow parameters derived from Steps 1 to 4 above were compared with the available hydraulic data (Brabets and Ourso 2013). As part of this flow calibration processes, the initial Manning's n coefficient (0.04) was adjusted to better fit the measurements at the USGS station. In the end, the most suitable Manning's n coefficient for Slate Creek was determined to be 0.053, which was very similar to the literature value of 0.05 provided for mountain streams with cobbles with large boulders (Chow 1959). Pictures taken during field work indicated that the creek bottom does in fact have many rocks, further justifying this assumption.
6. Using the developed Manning equation, simulated values at the USGS station were estimated at 1.45 cfs for flow (compared to the observed flow of 1.5 cfs [Brabets and Ourso 2013]) and 1.31 ft/s for velocity (compared to the observed velocity of 1.3 ft/s [Brabets and Ourso 2013]).

While there is a lack of field data for flow parameters, the method described above including the estimated stream geometry adequately estimated flow conditions at the USGS monitoring station. This methodology was applied to the other model segments. Table A-1 presents the calculated flow and velocity for each segment. Based on the calculated flow and flow mass balance calculation, additional diffuse flows were estimated. These potential diffuse flows were calculated and used as the modeled mixing ratio.

Table A-1. Estimated flow and velocity for each model segment

Sampling Location	Estimated Flow (cfs)	Estimated Velocity (ft/s)	Measured Depth (cm)
05SC01	0.27	0.84	4
05SC04	0.46	0.80	5
05SC05	0.45	0.80	5
05SC06	4.50	0.80	14
05SC07	7.29	3.50	16
05SC08	7.80	4.52	16
05SC09	8.50	4.05	20
05SC10	3.34*	3.87	15

*The calculations indicated a losing stream reach at this segment. During the model simulation, model results from 05SC09 were continued through 05SC10 segments without any special treatment, such as the modification of the flow ratio to reflect the losing flow. It was assumed that all solutes contained within the lost flow were transported through the sediment, thus, no effect on the instream concentration.

In addition, sampling conducted in August 2005 identified seep and tributary inputs to Slate Creek downstream of the headwaters. Flows associated with these sources were estimated. Based on field pictures, the seep was contributing very low flow rates. This flow was visually estimated to be 1.5% of the mainstem flow recorded at the 05SC04 monitoring location. Visual interpretation of the field pictures indicated a slightly higher, but still fairly low, flow rate associated with the tributary input.

To verify contributions of these two inflows, chloride and conductivity data were examined. The conservative (not reactive) chloride data indicated fairly high concentrations of chloride observed in both the seep (25 mg/L) and the tributary (22 mg/L), compared to station 05SC04 that had only 1.1 mg/L chloride, which was almost the same as the background concentration (1.2 mg/L at 05SC01). Conductivity also shows the same trend; the concentration at 05SC04 is slightly higher than the headwater conductivity. Based on these analyses, it was concluded that, although the seep and the tributary directly flowed into the mainstem, the solute loads were not

significant; therefore, the associated flows had to be low (higher flows would result in higher loads to the mainstem, which would have resulted in higher chloride and conductivity measurements at 05SC04). However, the previously derived flow at 05SC04 indicated that there was a flow contribution at an unknown location(s) above 05SC04. The diffuse flow contribution was estimated to be as much as 40% of the main stem flow volume, thus, additional flow volume associated with a diffuse input was assigned to the model segment before 05SC04. Without further available data, the assigned flow volume was assumed to be a combination of the tributary (approximately 10%) and diffuse flow (subsurface flow).

Boundary Conditions – Headwaters (Station 05SC01)

Ritchie et al. data collected at 05SC01 were assigned as the headwater water quality boundary conditions in the model (2013). The headwater boundary condition is used to characterize inputs from undisturbed areas in the model. Station 05SC01 was selected as it is the only station available that represents background conditions (upstream of all mine impacts). These data include metals with major cations and anions and other parameters critical to simulate metals, as identified in Table A-2.

Table A-2. Boundary conditions at headwaters (station 05SC01)

Alk	As(III)	As(V)	Ca	Cl	Fe(II)	Fe(III)	K	Mg ₂	Na	pH (±0.5)	Sb	SO ₄ ⁻	Temp °C	Al
73.1	0.5	5.2	22.4	1.2	0.1	0.02	0.26	11.2	0.83	7.5	4.2	28	8.8	3.8

Note: Alk = alkalinity, As = arsenic, Ca = calcium, Cl = chloride, Fe = iron, K = potassium, Mg₂ = magnesium, Na = sodium, Sb = antimony, SO₄⁻ = sulfate, Temp °C = temperature in degrees Celsius, Al = aluminum (these are consistent for all tables below); all chemical units are mg/L except for Al, As, and Sb are in µg/L and alkalinity is mg/L as calcium carbonate (CaCO₃).

Dissolved oxygen (DO)

Dissolved oxygen in the headwater solution was assigned to be at equilibrium with the atmospheric pressure of oxygen (0.2 standard atmosphere [atm]). This assumption was made through evaluation of the available DO and temperature data simultaneously collected at the USGS sampling location on different dates (Brabets and Ourso 2013). Figure A-3 compares the observed DO and the calculated saturated DO based on the stream temperature using the method described in Standard Methods (APHA 1992).

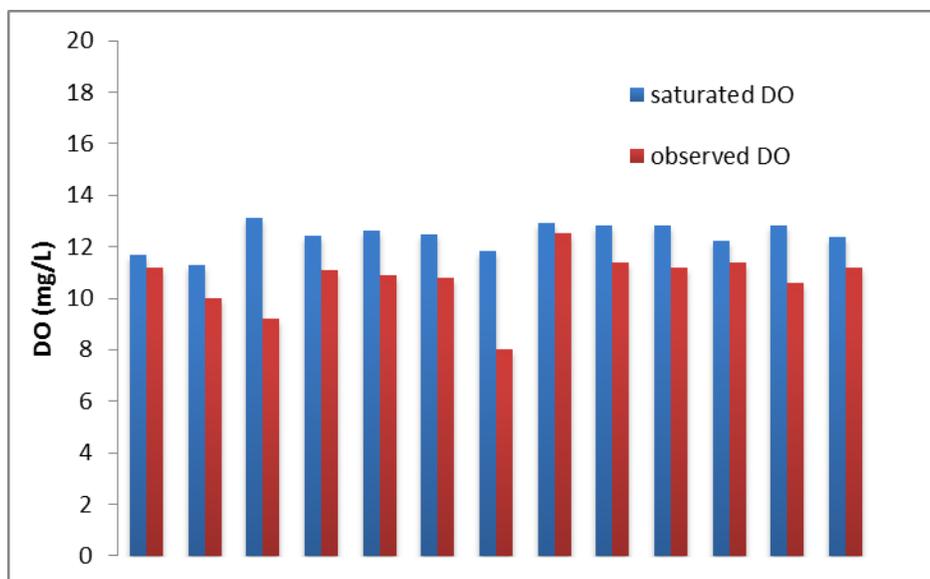


Figure A-3. Comparison of observed DO and calculated saturated DO at USGS 15547575.

The observed and calculated saturated DO values were similar although the observed DO showed slightly lower concentrations, but generally above 8 mg/L (Figure A-3). This lower observed DO could be attributed to different biotic and abiotic DO-controlling mechanisms, such as mixing with potentially lower DO groundwater flow, biological consumption of DO, redox reactions, and slow kinetic oxygen reaeration; however, generally speaking, the data indicated that the solution was close to the DO saturation level and maintained an oxidized condition.

Boundary Conditions – Seep (Station 05SC02)

Ritchie et al. identified a mine waste seep as an input to Slate Creek; therefore, this source was included in the model using a boundary condition. Station 05SC02 was a sample from the mine waste seep and these data were used to represent the boundary water quality conditions for the seep (Table A-3; Ritchie et al. 2013). As described above, the seep flow was estimated at 1.5% of the mainstem flow volume at 05SC04.

Table A-3. Boundary conditions for the seep (station 05SC02)

Alk	As(III)	As(V)	Ca	Cl	Fe(II)	Fe(III)	K	Mg ₂	Na	pH (±0.5)	Sb	SO ₄ ⁻	Temp °C	Al
0	14	165	69.3	25	50	184	0.62	52.6	0.5	2.8	124	2,004	12	6,490

Note: all chemical units are mg/L except for Al, As, and Sb are in µg/L and alkalinity is mg/L as CaCO₃.

Boundary Condition – Diffuse Inflow near Tailing Piles (input located near Stations 05SC05 and 05SC06)

Minerals existing within the Slate creek watershed contain acid-forming sulfide minerals, such as pyrite (FeS₂), and associated arsenopyrite (FeAsS) and stibnite (Sb₂S₃), all of which have the potential to impact the creek's water quality (Ritchie et al. 2013). Furthermore, Eppinger et al. describe that the vein faults within the watershed are classified into three types: (1) quartz-arsenopyrite-pyritescheelite-gold, (2) galena-sphalerite-tetrahedrite-pyrite-chalcopyrite with siderite gangue, and (3) stibnite-quartz veins free of other sulfides (2000). Based on this minerals information, a general water quality characteristic of the leachate around and from the tailings was quantified for a modeling input from this source (represented as a boundary condition). Stations 052SC05 and 05SC06 are instream stations located adjacent to and just downstream of the tailing piles (see spatial representation in Figure A-1). Because these data are ambient stations and do not characterize the input to the system, these were not used directly to represent this boundary condition. Rather, characteristics of the input or leachate itself were determined and input to the model near stations 052SC05 and 05SC06.

In order to estimate the leachate chemistry, the following modeling procedures and assumptions were applied:

- Initially, a general rainfall chemical condition was simulated as the chemistry drives the initial subsurface solution condition once it is infiltrated into the soil. The rainfall chemistry was assumed to be equilibrium with atmospheric CO₂ and O₂ conditions. The model-assigned temperature was derived by averaging the air temperature from the month leading up to the sampling date of August 5, 2005 (12.9 °C). An average rainfall pH of 5.15 in the Alaska region (Bormann et al. 1989) was also assigned to the rainfall solution. The simulated rainfall carbon content was input into the subsurface and used to represent the initial subsurface solution. Other chemical elements were assumed to be minor.
- Scorodite with an adjusted equilibrium constant was incorporated as one of the potential mineral compositions that can be generated if the target saturation index was attained in the tailings (Langmuir et al. 2006). Gypsum and jarosite were also incorporated in the model to potentially regulate chemical elements within the tailing solution in the model. Although there was no direct measurement of the potential outflow from the tailing, these two minerals were cited in literature as potential existing minerals in mine effluent (Wisskirchen et al. 2010; Kumpulainen et al. 2007). The saturation index (SI) calculation of the seep indicated their potential presence (jarosite being oversaturated [SI = 6.82] could be related to slow kinetics, while gypsum is undersaturated [SI = -0.82], but close to SI = 0). Ferrihydrite was also

included in the model to simulate potential iron precipitation and provided the adsorption surface for the simulated chemicals.

- Cation exchange capacity (CEC) of 6 milliequivalents per 100 g (meq/100g) based on SURROGO soils data was also incorporated into the model.
- Additional hydrous ferric oxide adsorption thermodynamic data were supplemented for carbonate and iron adsorptions from the PHREEQC database to simulate competitive adsorption reactions among the considered chemicals. The competitive adsorptions among these chemicals, especially the higher iron and carbonate concentrations in the source, could potentially control arsenic adsorption/desorption onto the iron oxide surface in subsurface soils (Appelo and Postma 2005).
- Existing minerals considered in the model were pyrite, arsenopyrite, stibnite, kaolinite, and calcite. Kaolinite and calcite were included as weathering of a primary aluminosilicate mineral, such as anorthite, existing as a part of feldspar observed in the Slate Creek watershed. Dissolved aluminum from kaolinite was allowed to precipitate as gibbsite if the solution became oversaturated with the mineral.
- The CO₂ pressure of groundwater is easily one or two orders of magnitude higher than atmospheric CO₂ pressure (~0.00035 atm). This is mainly because CO₂ is generated by root respiration and decay of labile organic material (Hanson et al. 2000); therefore, the subsurface CO₂ condition was set to 0.0026 atm based on a literature value of Alaska region (Brook et al. 1983).
- Without direct measurements of subsurface organic matter in and around the tailings, values were estimated from the organic matter content in stream sediments collected at the USGS sampling station. Mean dissolved organic matter (DOM) and particulate organic matter (POM) in saturated and unsaturated zones in soil have been calculated from data available in EPA's STORET database (Table A-4; USEPA 1996).

Table A-4. Organic matter data

Zone	POM (mg/L)	DOM (mg/L)
Unsaturated zone	4,798.5	20.32
Saturated zone	2,634	14.4

Notes: POM is particulate organic matter; DOM is dissolved organic matter.

However, not all of the organic matter presented in Table A-4 was assumed to participate in the redox reactions – rather, a small portion of the organic matter was assumed to be labile. Therefore, reactive organic matter was derived by applying the ratio between POM and DOM in Table A-4 to the observed percent weight-based the organic matter (1.8%) (converted to a mass-volume based, dissolved organic carbon [DOC] value). After the calculation, 0.005 moles per liter (mol/L) of CH₂O was assigned to the model as the labile organic matter existing in the tailings.

- The mixing ratio between the background groundwater solution (assumed to be the same as 05SC01 data) and the derived tailing solution were adjusted during calibration of the instream model. Additionally, the available oxygen within the tailings was adjusted to promote oxidation of the minerals.

The final model simulation yielded a pH of 6.4, 47 µg/L of dissolved arsenic, 855 µg/L of dissolved antimony, and 37 mg/L of dissolved iron in the tailing outflow solution. The purpose of this simulation was to estimate the potential solution condition at the edge of the stream (the interface between the sediment and stream water), where the potential reduced condition of the tailing leachate seeps into the more oxidized sediment layer, at which the redox condition changes from the subsurface reduced condition to a higher reduction potential (pE) value (pE of the tailing solution at this interface was set to 2.8, which was the same as the mining-related oxidation reduction potential (ORP) observed from the seep in July 2007 [Ritchie et al. 2013]).

Figure A-4 illustrates the transition from the reduced to the more oxidized condition, potential iron precipitation, and adsorption of the chemicals onto iron oxide (hydrous ferric oxide or HFO). The figure also shows the other chemicals (organic matter, other ions) and CEC that were considered in the simulation.

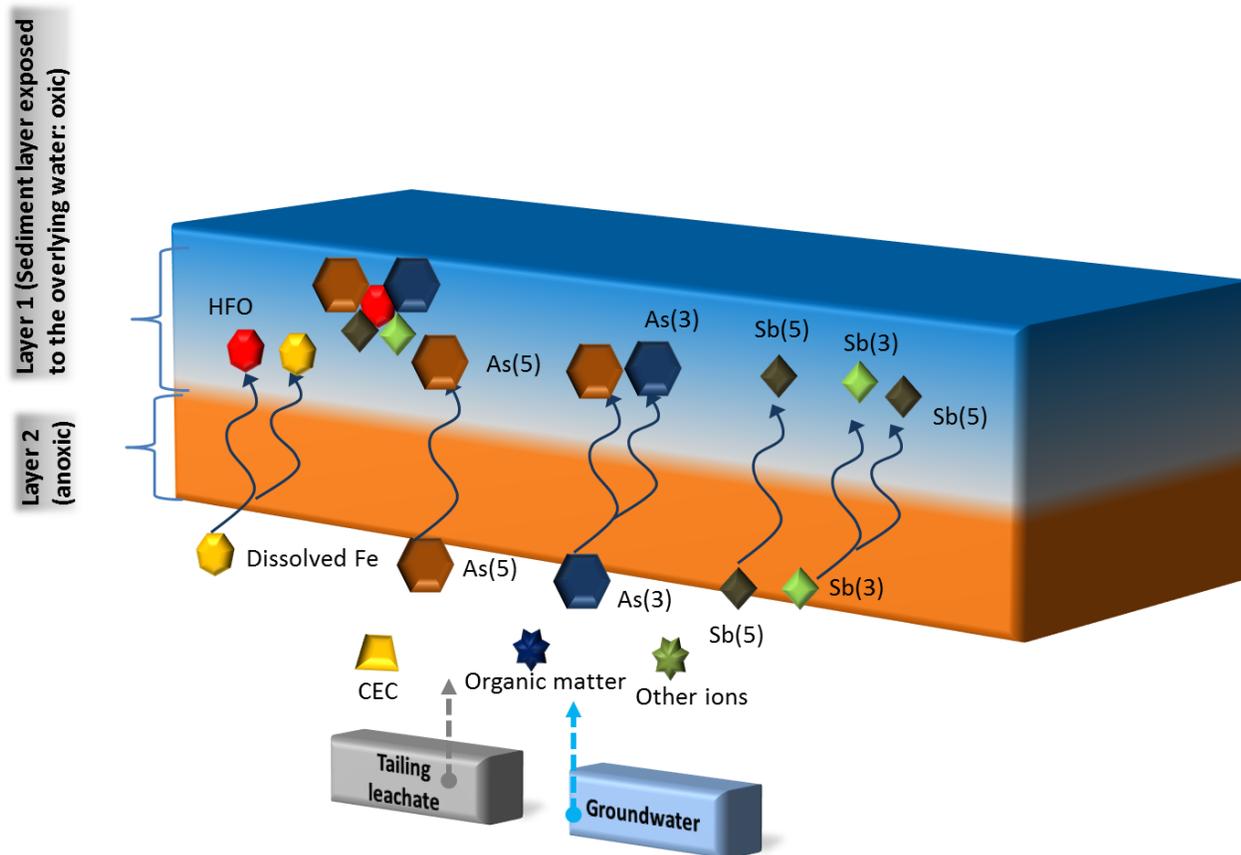


Figure A-4. Representation of the redox conditions and chemical interactions.

Boundary Conditions – Tributary (Station 05SC03) and Diffuse Input (input located upstream of Station 05SC04)

As described previously, the flow balance indicated an additional flow contribution to the creek besides the tributary input (associated with station 05SC03) contributing to the instream conditions that are represented by station 05SC04, which is located near the start of the tailings. To characterize these inputs as boundary conditions, during model calibration, 10% of the flow estimated at station 05SC04 was assigned as the tributary flow based on the visual assessment of the field pictures. Water quality conditions for the tributary input were assigned the values from station 05SC03, which sampled the tributary itself (Table A-5; Ritchie et al. 2013).

The field pictures also indicated that the tributary area appears to be near the mining affected area and higher metal concentrations indicated that as well. Therefore, the remaining diffuse flow contributing to instream station 05SC04 was considered similar to the subsurface upwelling flow generated through the mining area (see Section on Diffuse Inflow near Tailing Piles above). Specifically, the diffuse flow chemical solution was assumed to originate or flow through the mining affected area and was simulated using the tailing solution simulation described in the section above. The ferrous/ferric iron ratio was assumed to control the reduction potential conditions as indicated in other literature. This ratio was used to set the initial redox potential in the model.

Table A-5. Boundary conditions for the tributary (station 05SC03)

Alk	As(III)	As(V)	Ca	Cl	Fe(II)	Fe(III)	K	Mg ₂	Na	pH (±0.5)	Sb	SO ₄ ⁻	Temp °C	Al
98	7.8	3	59.9	22	9	4.4	0.42	31.9	0.52	6.1	407	171	10.7	9.5

Note: all chemical units are mg/L except for Al, As, and Sb are in µg/L and alkalinity is mg/L as CaCO₃.

Additional Water Quality Boundary Conditions (inputs located near Station 05SC07 and Downstream)

There were other locations where potential diffuse flows could exist as inputs to the creek, as described in the Hydraulic Configuration Section above. Once the modeled segments were beyond the tailing piles, there did not appear to be many additional inputs identified during field work (Ritchie et al. 2013). Therefore, concentrations for any additional diffuse flows included in the model to achieve mass balance were set equal to the observed values at the background station (station 05SC01) (associated with the headwater; Table A-2).

Model Processes

The PHREEQC model considers many interactions and reactions to simulate water chemistry. Some of the key processes that drive conditions within Slate Creek are described below.

In-stream Processes

The model's geochemical reactions within the channel were based on thermodynamics using EPA's MINTEQA database and additional kinetic reaction. To simulate and attain realistic stream chemical conditions, the model includes the following reactions:

- Trace metals chemical speciation, including other chemical elements
- Acid/base chemical reactions and pH simulations
- CO₂ gas ingassing/degassing
- Kinetic oxidation of dissolved ferrous
- Minerals precipitation/dissolution
- Adsorption/desorption based on diffuse double layer (DDL) modeling

In-stream temperature was also considered and simulated. The resulting stream temperature was used for all chemical reactions occurring within the stream. The stream components represented in the model are shown in Figure A-5. The subsections below discuss pertinent details on some of the reactions identified above.

Iron Kinetics

The kinetic reaction of the oxidation of Fe⁺² by oxygen (O₂) in water was simulated in the model and represented by the following equation (Singer and Stumm 1970):

$$\frac{dm_{Fe^{+2}}}{dt} = -(ka_{OH}^2 PO_2) Fe^{+2}$$

Where: k = a reaction rate

t = time (in seconds)

a_{OH} = activity of the hydroxyl ion

Fe⁺² = total molality of ferrous iron in solution

PO₂ = the oxygen partial pressure (in atm).

k was adjusted during calibration within the range of field values [$4.50\text{e}+12\sim 4.50\text{e}+14$ ($\text{M}^{-2}\text{atm}^{-1}\text{s}^{-1}$)] (Geroni and Sapsford 2011). Slightly higher k values [$1.75\text{e}+15$ ($\text{M}^{-2}\text{atm}^{-1}\text{s}^{-1}$)] were selected for the modeled segment associated with 05SC05 and 05SC06 during calibration.

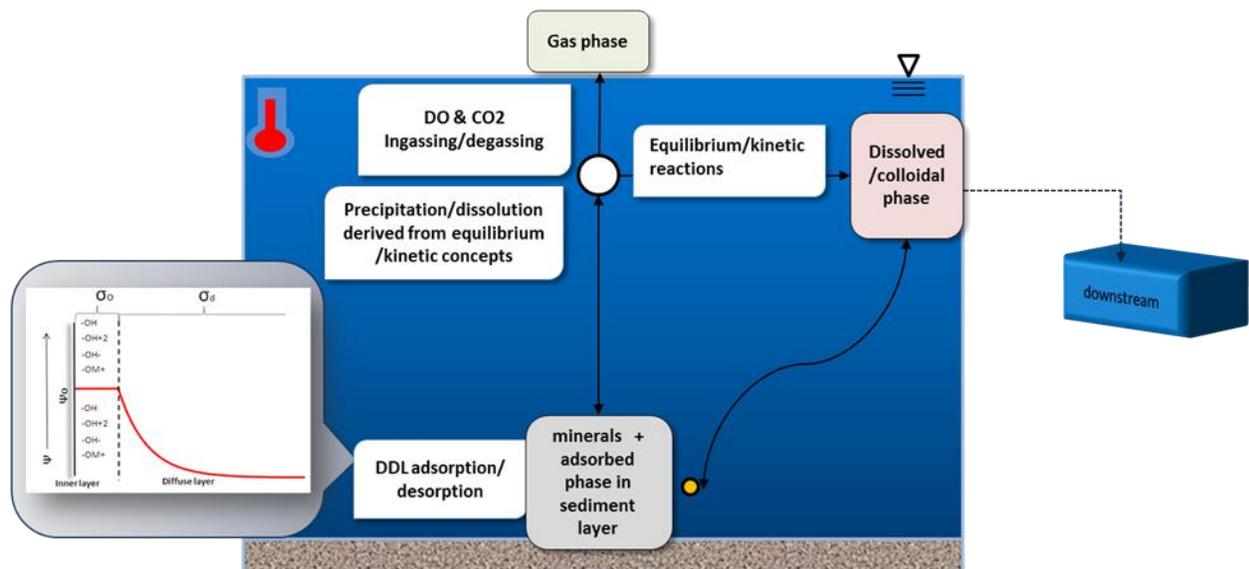


Figure A-5. Conceptualization of instream processes and functionalities.

Iron Precipitations

Once ferrous iron was transformed to ferric iron by the kinetic reaction, the newly generated ferric iron and the already existing ferric iron were subjected to chemical precipitation, depending on the solution conditions. The precipitation reaction of iron oxide was simulated as amorphous iron oxide or Ferrihydrite mineral in the model. SI was adjusted during calibration to simulate the slow kinetics of ferric iron precipitation in the solution.

Temperature Influence on Arsenic Adsorption/Desorption

In addition to the pH influence on arsenic adsorption onto iron oxides, literature indicates the temperature effects of arsenic adsorption. This is due to sorption of arsenic onto iron oxides, especially hydrous ferric oxide (HFO), which is known to be an exothermic process (Gammons et al. 2007), thus, more adsorption occurs as temperature decreases and less adsorption occurs as temperature increases. As Slate Creek temperature is generally low, an average of 10 °C for 2005 data and 7.8 °C for 2007 data (Ritchie et al. 2013), the low range of observed temperatures could influence the affinity of arsenic to the iron oxide adsorption surface.

Therefore, site-specific enthalpy data for the adsorption/desorption reaction were developed with the observed arsenic concentrations in the sediment and water column and temperature data. Using these data, the plot in Figure A-6 was generated. The slope of the regression line was used to calculate the absorption enthalpy. The enthalpy value derived by this method was -749 kilojoules per mole (kJ/mol); the negative value indicates that the adsorption of arsenic is indeed an exothermic process. The derived value was assigned to the model during simulations. Antimony could show a similar reaction tendency, but due to the lack of literature and previous studies on this topic, it was not investigated further.

CO₂ Degassing/Ingassing

Over- and under-saturated CO₂(g) in the solution is subjected to either ingassing or degassing reactions. CO₂(g) transfer between the water and air interface can be an important reaction to control the pH condition of the solution. During model calibration, the existing solution CO₂(g) level was identified in the model. All of the CO₂(g) was oversaturated compared to the atmospheric CO₂ pressure level (0.00035 atm); therefore, during calibration, partial degassing was simulated by adjusting the log partial pressure of CO₂(g). CaCO₃ formation due to pH increases from degassing reactions was also included in the model as one of the pH control mechanisms.

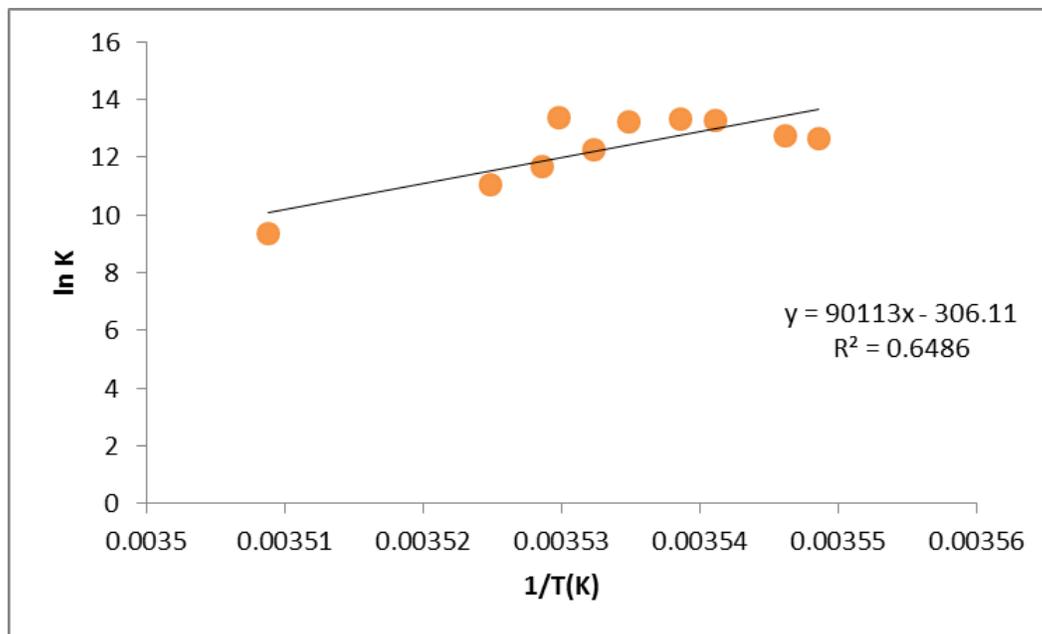


Figure A-6. Regression plot for calculation of absorption enthalpy.

Sediment Processes

The streambed in the model was represented as active sediment and was thought to be either amorphous iron oxide or Ferrihydrite. Arsenic and potentially antimony are chiefly associated with Ferrihydrite or HFO in Slate Creek (Ritchie et al. 2013). Other literature (Gault et al. 2005) also suggested a strong adsorption affinity of arsenic onto HFO. Thus, the incorporated HFO surface complexation (Dzombak and Morel 1990) was used for the adsorption/desorption of arsenic and antimony, and other simulated ions. The potential iron dissolution from HFO was also simulated as a source to alter the instream iron concentration. To incorporate the iron sediment data in the model, the observed iron sediment data were converted from mass-based to volume-based concentrations using stream bottom porosity of 0.8 (Lerman 1979) and iron oxide density (3.5 g/cm^3) (Dzombak and Morel 1990). Additionally, the actual reactive iron that participates in the simulation, such as amorphous iron oxide or Ferrihydrite, were estimated to be 10 % of the observed iron sediment data (Parkhurst and Appelo 2002; Zhu and Anderson 2002).

Iron Sediment Conditions

Figure A-7 presents the iron content in the sediment and the solution concentration of dissolved iron (filtered through $0.45 \mu\text{m}$) along Slate Creek. The sediment data indicated higher iron sediment content within the sediment samples collected in the seep, tributary, and 05SC06 and 05SC07 locations. Other sampling locations (05SC04, 05SC05, 05SC08, 05SC09, and 05SC 10) show very similar iron sediment concentrations as the headwater station (05SC01). 05SC06 is the location of the first sample taken below the disturbed tailing area. Considering the proximity to the tailings, it is reasonable to assume that the iron sediment data show iron precipitation affected by the tailings at 05SC06 and the swift sedimentation processes around the affected area. Dissolved and some colloidal size iron from the tailings appear to be transported downstream and deposited between 05SC06 and 05SC07, resulting in higher iron sediment concentrations at these locations.

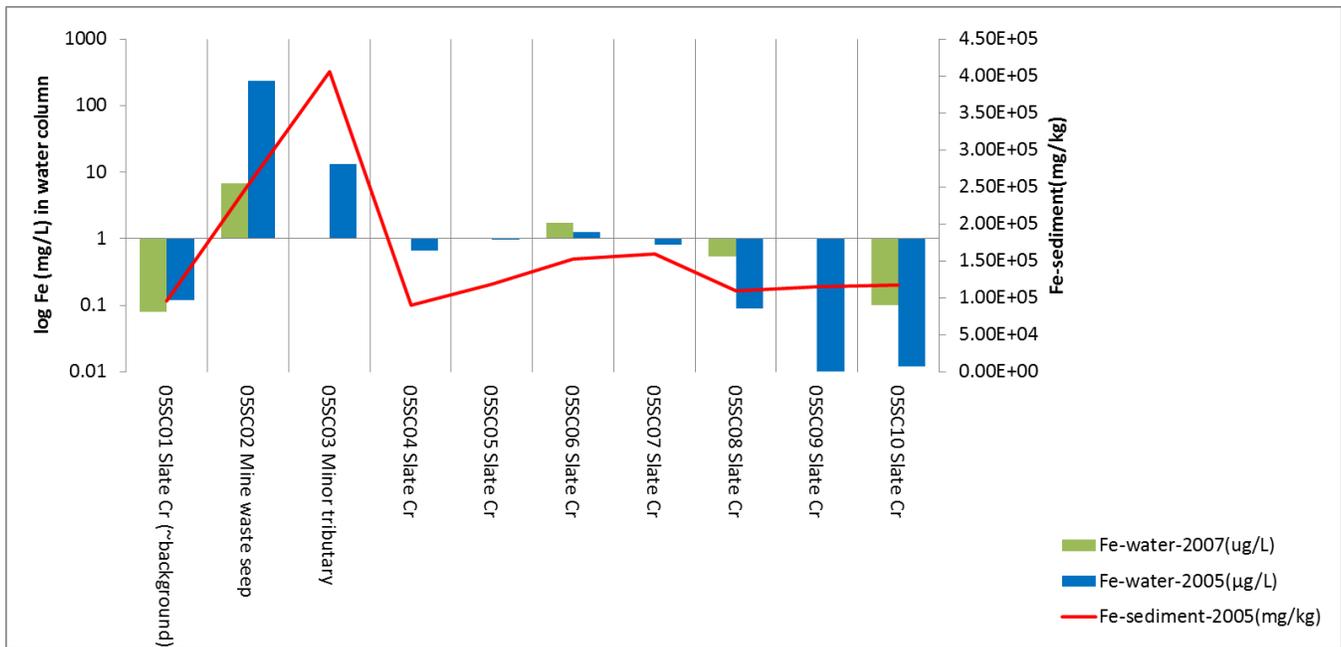


Figure A-7. Iron concentrations in the water and sediment.

To verify the assumed swift iron sedimentation at or around 05SC06, the potential deposition of iron oxide was calculated using the equation below.

$$\frac{dm Feox}{dt} = -k \times \frac{Feox}{d}$$

Where: Feox= iron oxide (mg/L)
 d = depth (cm)
 dt = time (in seconds)

Feox was derived from the calibrated model results at the model segment associated with 05SC06. The model indicated that the highest iron oxide mineral (25 mg/L iron) was being generated at this segment. Literature value of iron flocs’ setting velocity of 0.8 millimeters per second (mm/s) at 10°C was used in the model (Fair et al. 1986). The calculation with the travel time derived from previously estimated flow indicated that all of the newly generated iron oxide was deposited within the simulated reach (the observed stream depth was 14 cm). The settling rate at high ionic strengths can be very rapid because of high collision frequency (Evangelou 1998). Thus, the rapid sedimentation of high iron concentrations with other dissolved ions affected by the tailing solution can be expected. Additional colloid flocculation processes also promote the deposition.

Model Results

Model simulation results are shown below and compared to the observed data (Figure A-8). Although limited data were available from the sites for comparison, results indicate that the model assumptions and selected parameters described in the previous sections reasonably represent the conditions in the Slate Creek, when comparing all parameters below and especially arsenic, antimony, and iron (Figure A-8). Other simulation results were also provided to evaluate the ability of the model to represent the water quality conditions and the selected source mixing ratio.

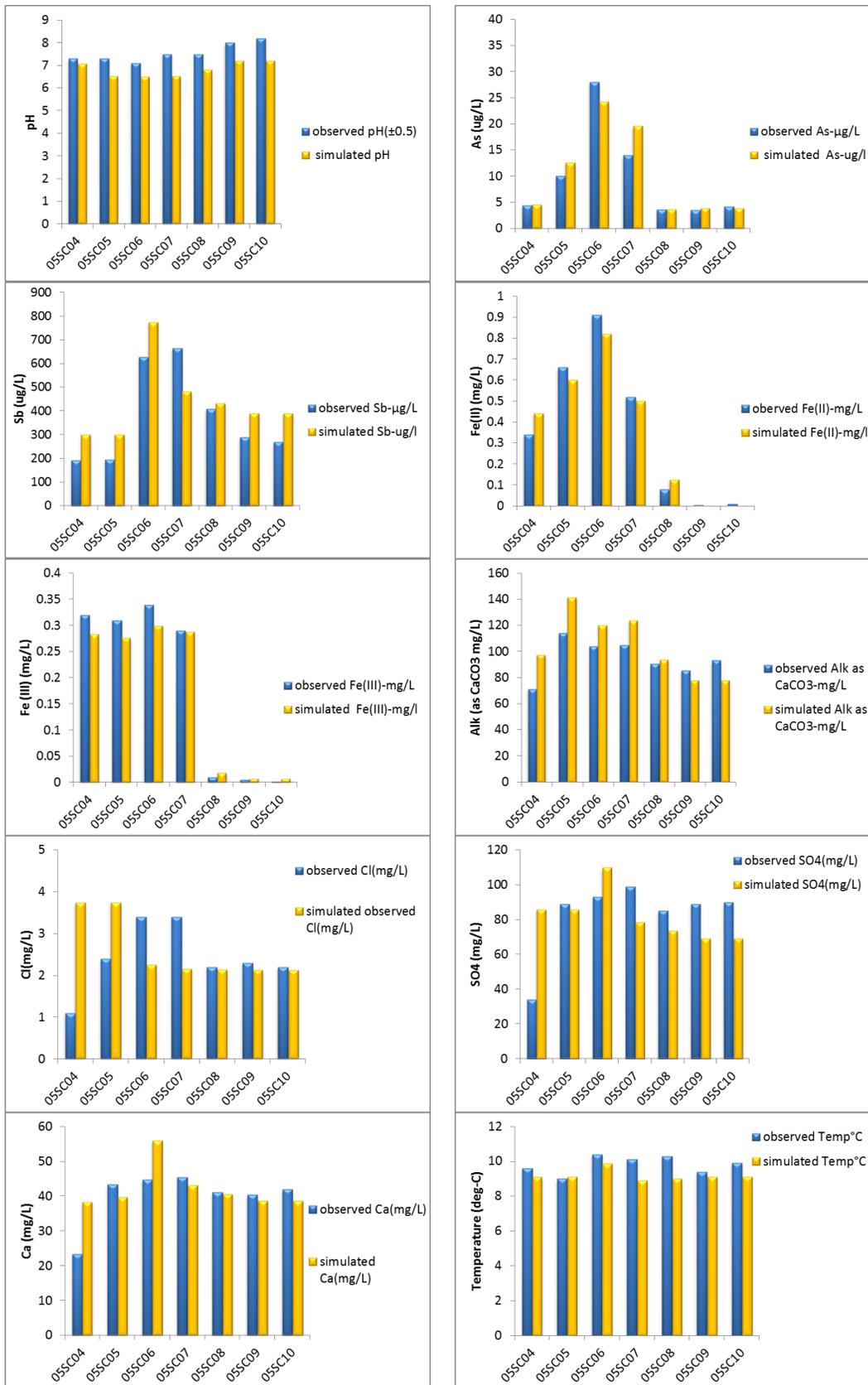


Figure A-8. Comparison of modeled and observed water quality parameters.

Appendix B

Pending information on the response to comments; to be completed after the public comment period.