

Forward: Precision and Relative Percent Difference in the 2017-2019 Multi-Agency Baseline Monitoring Dataset

Alaska Department of Environmental Conservation

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In late 2019 the Alaska Department of Environmental Conservation (ADEC) evaluated a subset of water quality data from the Kenai River for inclusion in the 2020 Integrated Report. The subset of data was sourced from the Kenai River Multi-Agency Baseline Monitoring program (hereafter referred to as Baseline), managed by the Kenai Watershed Forum. The data covered a period from 2107 to 2019 and included dissolved metals (As, Cd, Cr, Cu, Pb, and Zn), total metals (Ca, Mg, and Fe), nutrients (N and P), and pathogens from 13 sites along the Kenai River and 9 sites in tributaries.

Quality control thresholds were outlined for the Baseline program in a series of Quality Assurance Project Plans (QAPP). Starting in the 2012 QAPP¹, a minimum of 10% of the field samples were required to have a paired duplicate (QA) sample. These QA samples would be collected during both the spring and summer sampling events. Also, the replicate sample(s) would be rotated among the 7 monitoring teams (see pg. 31, KWF 2012). Precision was to be evaluated by calculating the relative percent difference between a routine sample and its QA sample. The RPD was not to exceed 20% for dissolved metals (pg. 14-18, of KWF 2012). RPD is defined as follows:

$$RPD = \frac{(A - B)}{(A + B)/2} * 100$$

Where A is the routine sample and B is the duplicate, or QA sample (KWF 2012).

A standard quality assurance evaluation of the Baseline data revealed that dissolved zinc and copper data did not meet the quality control thresholds set for the project. Between 2007 and 2009, 67% (6 of 9) of the paired QA samples for dissolved zinc exceeded the 20% RPD (Table 1), and 56% (5 of 9) exceeded for copper. It was also noted that the number of QA samples was insufficient (<10% of samples) to evaluate dissolved metals in the Kenai River mainstem for multiple years because a significant number of QA samples were collected at tributary sites and were not representative of the mainstem.

Dissolved cadmium, chromium, arsenic, and lead from the 2017-2019 Baseline dataset were accepted for inclusion in the IR by ADEC. The RPD percent failure for cadmium and chromium were 0% and 10% respectively. Arsenic and lead both had RPD failures of 30%, however the observed values were an order of magnitude less than the applicable water quality criteria (18 AAC 70) and were therefore accepted. The cadmium, chromium, arsenic, and lead data will be uploaded to the EPA Water Quality Exchange (WQX).

Based on the frequency of RPD exceedance in the 2017-2019 data, it was determined that dissolved zinc and copper from the 2017-2019 dataset could not be included in the 2020 IR. This decision was made

¹ The 2012 and 2019 QAPP were applied to the 2017-2019 dataset provided.

after the ADEC QA officer reviewed the data, and the ADEC WQSAR Program Manager discussed the data issues with the Region 10 EPA lead. KWF was contacted about the issue (October 12th, 2020), and options for moving forward were discussed.

Table 1. Relative percent difference (RPD) for routine samples and their paired duplicate sample for the Kenai River Multi-Agency Baseline Monitoring Program from 2017-2020. Non-detects (ND) are indicated. One half of the lab provided method detection limit was substituted for ND's for RPD calculations.

DATE	RM	Name	Type	Zn (ug/l) Routine	Zn (ug/l) Duplicate	RPD	>20
4/25/2017	0	No Name Creek	Tributary	82	110	29%	Yes
7/25/2017	1.5	City Dock	Mainstem	39	44	12%	No
7/25/2017	36	Moose River	Tributary	15	46	102%	Yes
4/24/2018	1.5	City Dock	Mainstem	51	76	39%	Yes
4/24/2018	19	Slikok Creek	Tributary	60	95	45%	Yes
7/31/2018	0	No Name Creek	Tributary	157	123	24%	Yes
4/30/2019	1.5	City Dock	Mainstem	89.9	110	20%	No
4/30/2019	19	Slikok Creek	Tributary	74.4	ND	192%	Yes
7/30/2019	0	No Name Creek	Tributary	5.53	5.31	4%	No
% Of paired samples with RPD >20%							67%

In 2021 ADEC initiated a two-year ambient water quality monitoring project on the Kenai River. The primary objective of this project was to evaluate dissolved zinc and copper levels on the Kenai River mainstem. The secondary objective was to incorporate additional quality assurance procedures to evaluate sampling methods for potential sources of contamination. The ADEC monitoring project incorporated 'clean hands, dirty hands' (EPA 1996) methods, field blanks, more frequent QA samples (4 per sampling event, i.e., >20% frequency), and the inclusion of total zinc and copper analysis. This project is ongoing, and a final report is expected in 2023. A 2021 field report is available on the ADEC website (see ADEC 2021).

References

- ADEC. 2021 Kenai River Water Quality Monitoring. Prepared by S. Apsens and J. Petitt. Alaska Department of Environmental Conservation, Division of Water, Soldotna, AK. 36 pg.
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- KWF. 2012. Quality Assurance Project Plan: Kenai River Watershed Monitoring Program. 2nd edition. Prepared for the State of Alaska, Department of Environmental Conservation, Division of Water. 56 pg.
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STATUS OF COPPER AND ZINC LEVELS THROUGHOUT THE KENAI RIVER WATERSHED



4/29/2021

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The Kenai Watershed Forum (KWF) is a 501(c)(3) non-profit and is recognized as the regional watershed organization of the Kenai Peninsula, successfully identifying and addressing the environmental needs of the region by providing high quality education, restoration and research programs. KWF is a dynamic organization dedicated to protecting the streams, rivers, and surrounding communities on the Kenai Peninsula.

Contents

LIST OF FIGURES.....	III
LIST OF TABLES.....	III
LIST OF ACRONYMS.....	III
PURPOSE.....	4
INTRODUCTION	5
METHODS	6
Copper and zinc sampling.....	6
Kenai River Baseline Water Quality Monitoring (KRBWQM)	6
Copper and zinc-specific sampling events.....	7
Sample Accuracy and Precision.....	7
2019 Hardness values.....	8
Mapping potential sources of copper and zinc	8
Potential sources on the Kenai River.....	8
Potential sources throughout the Kenai River watershed	8
RESULTS.....	9
Copper and zinc sampling.....	9
Copper.....	9
Zinc.....	9
Variation among replicate samples	10
Mapping potential sources of copper and zinc	10
Potential sources on the Kenai River mainstem.....	10
Potential sources throughout the Kenai River watershed	10
DISCUSSION	11
Copper and zinc sampling.....	11
Copper.....	11
Zinc.....	12
Variation among replicate samples	12
Potential drivers of copper and zinc exceedances.....	12
Research recommendations	13
CONCLUSION	15
From information to action.....	16
DATA AVAILABILITY	16
REFERENCES	17
APPENDIX A: FIGURES	20
APPENDIX B: TABLES.....	27

LIST OF FIGURES

Figure 1. Kenai River watershed and water quality monitoring site locations during biannual (2000 – present) KRBWQM sampling events.....	20
Figure 2. 2019 - 2020 sampling locations.....	21
Figure 3. Kenai River mainstem sites copper concentrations and criterion (CCC) values.....	22
Figure 4. Kenai River tributary sites copper concentrations and criterion (CCC) values.....	23
Figure 5. Kenai River mainstem sites zinc concentrations and criterion (CCC) values.....	24
Figure 6. Kenai River tributary sites zinc concentrations and criterion (CCC) values.....	25
Figure 7. Kenai River Mainstem and tributaries, dissolved copper and zinc sample results by year.....	26

LIST OF TABLES

Table 1. Alaska Department of Environmental Conservation water quality standards and pertaining calculations.....	27
Table 2. Sampling site coordinates.	28
Table 3. Instances where zinc and copper data differs from Paired calcium and magnesium data.	29
Table 4. Copper and zinc levels and hardness-dependent criterion standards.....	30
Table 5. Relative difference levels (RPD) of duplicate samples by site and date.....	33

LIST OF ACRONYMS

ADF&G - Alaska Department of Fish & Game
ADEC - Alaska Department of Environmental Conservation
CCC - Criterion Chronic Concentration
CWA - Clean Water Act
EPA - United States Environmental Protection Agency
KPB - Kenai Peninsula Borough
KPFHP - Kenai Peninsula Fish Habitat Partnership
KRBWQM - Kenai River Baseline Water Quality Monitoring
KRCMP - Kenai River Comprehensive Management Plan
KRSMA - Kenai River Special Management Area
KWF - Kenai Watershed Forum
QAPP - Quality Assurance Project Plan
RPD – Relative Percent Difference
USFS - United States Forest Service
USGS - United States Geological Survey

PURPOSE

This field report highlights efforts conducted to assess levels of copper and zinc, as well as to their potential sources in surface water throughout the Kenai River watershed. These efforts are intended to complement and respond to the literature review submitted to ADEC in 2017 by the Kenai Watershed Forum under ACWA grant 17-06 ([Sires 2017b](#)). This field report will address the following questions:

1. What are the copper and zinc levels at specific water monitoring locations throughout the Kenai River watershed during spring and summer 2019-2020 sampling events?
2. Where are elevated levels of copper and zinc occurring throughout the Kenai River watershed during spring and summer 2019-2020 sampling events?
3. What is the status of mapping efforts of potential copper and zinc sources on the Kenai River and throughout its watershed?

INTRODUCTION

The Kenai River is a glacially-fed system located on the Kenai Peninsula. This 82-mile (132 km) river begins at the outlet of Kenai Lake and flows into the Cook Inlet, a branch of the Gulf of Alaska. Due to its size, the Kenai River is generally divided into three sections: the upper river (Cooper Landing at river mile [RM] 82 to Skilak Lake at RM 65), middle river (RM 50 at the outlet of Skilak Lake to RM 21 in Soldotna at the Sterling Highway bridge), and lower river (RM 21 to RM 0 at the mouth in the city of Kenai) (USGS 2021b). Several major glacial and non-glacial tributaries flow into the Kenai River (Figure 1).

The Kenai River watershed plays host to millions of Pacific salmon that utilize its waters for rearing and spawning habitat. These salmon are critical to Alaskan economy, recreation, and culture. As a result, the Kenai River watershed is a priority for conservation efforts, as it experiences significant anthropogenic pressures (Schoen et al. 2017). Over 20 years ago the Kenai Watershed Forum (KWF) identified a need for monitoring surface water quality parameters often influenced by development, impervious surfaces, boat use, and other sources. KWF established the Kenai River Baseline Water Quality Monitoring (KRBWQM) program in 2000 to track water quality changes over time. Twenty-two sites were chosen along the Kenai River mainstem and in its major tributaries with the intention of providing information on overall watershed conditions twice per year (Figure 1). Since inception a broad suite water quality parameters have been measured biannually including the metals copper, zinc, lead, arsenic, and others; nutrients such as phosphorus and nitrogen; hydrocarbon pollutants; fecal coliform bacteria; and intrinsic parameters such as pH, turbidity, conductance, and temperature.

As a result of ongoing monitoring efforts, increases in copper and zinc concentrations at some sites in the lower river were identified from 2010 through 2014 relative to previous sampling years (Guerron Orejuela 2016; Sires 2017a), warranting further investigation and more intensive monitoring for these metals. Zinc and copper are elements with both natural and anthropogenic sources, and when present in aquatic environments at high levels these metals can potentially be of ecological concern (Skidmore 1964). Metals interacting with aquatic organisms often exhibit greatest toxicity when in the dissolved phase (Gerhardt 1993), and can have harmful effects on Pacific salmon and their habitat. Sublethal levels of dissolved copper commonly found in urban aquatic systems have been shown to disrupt salmonid olfactory function (Tierney et al. 2010), behavior (Goldstein et al. 1999; Scott and Sloman 2004), and survival (McIntyre et al. 2012), primarily in freshwater. Chinook salmon (*Oncorhynchus tshawytscha*) have shown increased susceptibility to mortality from elevated zinc levels during early life stages- a critical period of time in development (Chapman 1978).

Effective toxicity of dissolved metals varies with environmental conditions, particularly water hardness. Hardness is used to calculate aquatic toxicity criteria for many dissolved metals because magnesium and calcium compete for metals binding sites on the fish gill (Galvez 1998). Copper and zinc exceedances are identified when their levels are compared to a hardness-dependent freshwater criterion chronic concentration (CCC), which varies with calcium and magnesium concentration (Table 1) (ADEC 2008).

Through grant funds provided through the Alaska Department of Environmental Conservation (ADEC) and matching funds from KWF, KWF identified four tributary and three mainstem sites in addition to the standard biannual KRBWQM sampling sites throughout the Kenai River watershed for supplemental sampling in the springs and summers of 2019-2020 (Figure 2). This report presents results the supplemental sampling events in tandem with results from the biannual KRBWQM events in 2019-2020.

Additional efforts to identify potential sources of copper and zinc throughout the Kenai River watershed were initiated in 2019-2020 and are reported here. These efforts included a fieldwork component in which five river trips were conducted in order to photograph potential zinc and copper sources visible

from the Kenai River mainstem. Photos from these trips were incorporated into a GIS shapefile established to document adjacent potential sources of these heavy metals including impervious surfaces, boat landings, and wastewater discharge. In addition to KWF's field imagery, St. Mary's University of Minnesota Geospatial Services was contracted to develop a draft ArcGIS database of sources potentially related to copper and zinc pollution. The geodatabase is intended to be of use in future monitoring efforts and potentially in the production of a future decision support tool.

METHODS

Copper and zinc sampling

Water quality sampling efforts for dissolved copper and zinc in 2019-2020 targeted sites that have been monitored biannually since the year 2000 as part of the Kenai River Baseline Water Quality Monitoring (KRBWQM) project, as well as new additional sites targeted to explore spatial trends in dissolved copper and zinc concentrations (referred to here on as “copper and zinc-specific sampling events.” In total, these sites comprise ten sites on the Kenai River mainstem and nine tributary sites (Figure 1).

Note: all river miles listed throughout document are in reference to the Kenai River mainstem. River miles listed for tributaries reference their confluence river mile on the mainstem of the Kenai River. Sampling site names were chosen based on sampling location; their corresponding river miles can be found in Table 4.

Kenai River Baseline Water Quality Monitoring (KRBWQM)

Kenai Watershed Forum conducted biannual KRBWQM events in 2019 and 2020. Sampling events are of a cooperative nature and require the participation and/or financial contributions of several agencies and organizations including:

- Alaska Department of Fish and Game
- City of Kenai
- City of Soldotna
- Cook Inlet Aquaculture Association
- Alaska Department of Environmental Conservation
- Alaska Department of Natural Resources
- Kenai Peninsula Borough
- Kenai Watershed Forum
- United States Fish and Wildlife Service
- United States Forest Service
- Local Kenai Peninsula volunteers

Due to logistical and safety constraints as a result of the COVID-19 pandemic, spring KRBWQM sampling did not occur in spring 2020.

The twenty-two sites in the KRBWQM sampling program were originally selected to represent the Kenai River watershed's ambient water quality conditions. Samples in 2019-2020 were analyzed for hydrocarbons, total suspended solids, phosphorus and nitrogen, fecal coliform, and metals (total and dissolved). Values reported in this document include concentrations of dissolved copper, zinc, magnesium, and calcium. Sample locations for the selection of data included in this report are presented in Table 2,

and sample dates are included in Table 4.

After a training session, sampling participants were split into small groups and sampled 2-5 sites by foot or boat. Sample collection timing coincided with an outgoing tide to reduce potential saltwater contamination of samples in the lower river. Individuals collecting samples by foot waded into the water until the water depth was approximately two feet and the participant was offshore in flowing water while still maintaining personal safety. For sites accessed by boats, water samples were taken from the bow while the boat faced upstream. Prior to sampling, all bottles were labeled with site and river mile; sampling team name; date and time; and parameter. Samples were collected by facing upstream, wearing clean gloves, removing the bottle seal, inverting the bottle and plunging it approximately one foot below the water surface. The bottle was then turned 90 degrees to allow water to fill at that depth. All bottles were stored in insulated coolers with ice packs to keep at 4°C and shipped via Grant Aviation to Anchorage. They were retrieved and analyzed by SGS North American, Inc (Anchorage, AK) within the holding time of each sample. Copper and zinc analyses were performed by SGS in Anchorage, while calcium and magnesium analyses were performed by ALS Environmental of Kelso, WA. These procedures follow the protocols established in a Quality Assurance Project Plan (QAPP) originally approved by ADEC in 2001, later revised and approved by ADEC again in 2013 and 2019 (ADEC 2020a). Parameter values were reported digitally; data entry and management was done in Microsoft Excel and R (R Core Team 2021). Hardness and hardness-dependent freshwater CCC criteria were calculated using ADEC-provided equations shown in Table 1 (ADEC 2008).

KRBWQM data from 2019-2020 described in this report includes all mainstem and tributary sites including and below river mile 23 (Swiftwater Park), as well as data from sites at the outlet of Skilak Lake and Jim's Landing, which are included as reference sites presumed to have chemical water quality parameters minimally affected by anthropogenic influence. Further details on historical KRBWQM results and protocols can be found in the project's most recent summary report (Guerron Orejuela 2016).

Copper and zinc-specific sampling events

In addition to the long-running biannual KRBWQM sampling events, in 2019 and 2020 KWF staff and volunteers also conducted water quality sampling specifically focused on dissolved copper and zinc concentrations. Sites for these sampling events included four sites in the upper reaches of tributaries and three mainstem Kenai River locations not regularly targeted in previous years (Figure 2).

Tributary sites were selected based on their historically-elevated levels of copper and/or zinc (Sires 2017b) as well as their location above most potential anthropogenic influence. On the Kenai River mainstem, the Slikok Creek confluence site was chosen in order to compare the levels of copper and zinc found in the mainstem to those within the Slikok Creek tributary. The Skilak Lake outlet and Jim's Landing sites were chosen as control sites as they are located upstream of the majority of development along the Kenai River and would provide relative background levels away from most anthropogenic influence. Jim's Landing is a designated boat launch utilized solely by recreationists using drift-only (non-motorized) boats.

All sampling procedures aligned with the ADEC-approved 2019 Quality Assurance Project Plan (KWF, 2019). Results for copper, zinc, calcium, and magnesium concentrations were reported digitally; data entry and management was done in Microsoft Excel and R Studio. Hardness and freshwater CCC values were calculated using ADEC-provided equations shown in Table 1 (ADEC 2008).

Sample Accuracy and Precision

To explore the degree to which an individual grab sample is representative of dissolved copper and zinc

concentrations, a total of fifteen replicate samples were collected and analyzed from sampling events in 2019-2020. Replicate samples were collected by the same personnel, with identical technique, within five minutes of each other. Relative percent difference (RPD) between replicates was calculated from the resulting values of each metal analyzed and described in context of the QAPP data quality objectives.

2019 Hardness values

As standard practice, zinc and copper data is synchronous in space and time with paired calcium and magnesium data used to calculate hardness and associated CCC values. However, for a total of five sites in two sampling events (May 22, 2019 and July 24, 2019), calcium and magnesium data was not available. Thus for these events, CCC criteria were instead calculated using calcium and magnesium results obtained from other sampling events with closest spatial and temporal proximity (see Table 3 for details).

Mapping potential sources of copper and zinc

Potential sources on the Kenai River

Throughout the summer of 2019, five photography trips were conducted by raft or motorboat along all sections of the Kenai River main stem to document parcels containing potential copper and zinc sources. This task was completed using Ricoh WG-6 digital cameras, which were equipped with GPS and aspect functionality. Two photographers took photos of each parcel with a potential metal source; one photographer was assigned the river-right (RR) bank while the other was assigned the river-left (RL) bank. Photos were taken directly out from the potential source, perpendicular to the bank of the river. Side channels diverting from the mainstem of the Kenai River were floated or boated as well. The geotagged photos are intended to serve as a reference for future work to identify locations and assess potential sources of copper and zinc in greater detail, and also serve as an archival set of observations to compare future photo transects.

Potential sources throughout the Kenai River watershed

A literature review conducted by KWF in 2017 (Sires 2017b) identified potential sources of copper and zinc throughout the Kenai River watershed, which can be described generally as contributors common to watersheds containing urban and suburban environments (Matthiessen et al. 1999). Potential sources of copper included brake pads/vehicles, pesticides/herbicides, roofing/metal plating, mining activity, boat hull coatings/anti-fouling agents, municipal wastewater discharge, natural mineral deposits, forest fires, air emissions, and decking/pilings. Similarly, potential zinc sources included galvanized metals, tire wear, motor oil/hydraulic fluid, fertilizer/pesticides/fungicides, natural mineral deposits, mining activity, forest fires, and brakes. Using results from the literature review, KWF contracted with St. Mary's University Geospatial (Winona, MN) to curate and prepare all available regional geospatial data potentially related to nonpoint sources of copper and zinc. All layers found were converted to a consistent projection and geodatabase format so that they may be integrated into a single map. Additionally, gaps in geospatial data availability that would likely be needed to fully assess copper and zinc sources were identified in the report.

RESULTS

Copper and zinc sampling

Note: all metals results are reported as dissolved metal concentrations.

Copper

Copper levels ranged from a low of undetected to one value that was above the CCC (criterion chronic concentration) value (Figure 3 and Figure 4). The highest observation of 8.16 µg/L was observed in the Kenai River mainstem at the Slikok Creek Confluence on July 24, 2019. It should be noted that the associated CCC value for this sampling event was based on hardness data from another nearby 2019 sampling event on the main stem Kenai River (see Table 3), thus the observation could be indicated as a potential, but unconfirmed, exceedance (see “Copper” in the Discussion section for further consideration).

The second greatest copper concentration in the data set, 3.91 µg/L, was observed at Upper Beaver Creek tributary on April 30, 2019, with other elevated observations also made at the City of Kenai Docks (July 21, 2020) and Upper No Name Creek sites (May 22, 2019). Hardness-dependent freshwater CCC criteria for copper ranged from a low of 2.31 µg/L (various sites) to a high of 121.31 µg/L at No Name Creek (July 21, 2020) (Table 2). No confirmed copper exceedances of CCC values were observed during any of the sampling events in 2019-2020.

Among all tributary and mainstem sites, the highest copper values observed were in the lower Kenai River region, closer to the developed Kenai/Soldotna area. Copper values > 2.5 µg/L were observed at the City of Kenai Docks mainstem site, in No Name Creek, and in Beaver Creek. All other copper values in the 2019-2020 dataset were below 2.5 µg/L.

Zinc

Zinc values ranged from a low of undetected to a high of 159.0 µg/L in Upper No Name creek on May 22, 2019 (Figure 5 and Figure 6). Hardness-dependent CCC values for zinc ranged from a low of 21.1 µg/L in Upper No Name Creek on May 20, 2020 to a high of 315.8 µg/L on April 20, 2019 at the City of Kenai Docks. Additionally, two observed zinc CCC values are atypical of historical data:

- Zinc CCC = 1069 µg/L at Lower No Name on July 21, 2020 (Zinc CCC range at this site, 2000 – 2018, is 3.25 – 42.25 µg/L)
- Zinc CCC = 628 µg/L at City of Kenai Docks on April 30, 2019 (Zinc CCC range at this site, 2014 – 2018, is 8.40 – 342.50 µg/L).

Although an exploratory analysis of hardness data 2000 – 2018 indicates possible evidence of marine influence at these sites (Meyer 2021b), the values listed above are still several multiples above the range of those observed 2000- 2018 and are therefore presumed unlikely to be representative of actual conditions.

Zinc exceedances of CCC criterion values were observed for a total of twelve samples. Zinc exceedances were observed at tributary sites including Upper No Name Creek, Lower Beaver Creek, Upper Beaver Creek, Lower Slikok Creek, Upper Slikok Creek, and Lower Soldotna Creek (Figure 5). Zinc exceedances in mainstem sites were observed at Cunningham Park, Upstream of Beaver Creek, Pillars, Soldotna Bridge, and Swiftwater Park (Figure 6).

As with copper, elevated zinc values were observed solely in closer proximity to the developed Kenai/Soldotna area. Zinc exceedances were not observed at the minimally anthropogenically-influenced sites of Jim's Landing, Skilak Lake Outlet, or Lower Funny River.

In the mainstem Kenai River sites, all zinc exceedances observed occurred during the April 30, 2019 sampling event, whereas timing of zinc exceedances in the tributary sites were variable and do not follow a visibly evident pattern.

Variation among replicate samples

A total of fifteen unique samples had paired copper and zinc replicate samples, from ten unique sites and seven unique dates. A relative percent difference of $> 20\%$ among replicate samples was observed in eleven out of thirty values, ranging from $0\% - 175\%$ (Table 5), with a mean difference of $38.9 \pm 13.6\%$ (mean \pm standard error) for copper and $34.8 \pm 14.3\%$ for zinc. The QAPP (ADEC 2020a) set a relative percent difference threshold for replicate samples of 20% , indicating that these eleven samples did not meet data quality objectives and the results should be flagged, interpreted conservatively, or not included in calculations of summary values (see Discussion).

Mapping potential sources of copper and zinc

Potential sources on the Kenai River mainstem

In total, 932 photos were taken of river-right parcels and 899 photos of river-left parcels with potential copper and zinc sources. These photos were imported into ESRI's ArcMap GIS 10.8.1 (ESRI 2020) program and converted to a points shape file. Photos included locations with elevated, light-penetrating walkways; building roofs; impervious surfaces such as roads and parking lots; significant bank erosion; boat launches; bridges; and RV parks. The shape file of geotagged photos is intended to serve as an archival document of potential sources of copper and zinc pollution, and may be useful to compare to similar transects in future years. The photos shape file may be particularly useful in the context of the additional GIS products described below.

Potential sources throughout the Kenai River watershed

The report from St. Mary's University of Minnesota Geospatial Services ([Robertson et al. 2020](#)), titled, "Kenai River Heavy Metal Pollution Source Data Mining Exercise for the Kenai Watershed Forum: Main Kenai River System", describes and curates a collection of fourteen data sources potentially useful for identifying sources of zinc and copper pollution. Listed below are all relevant geospatial datasets that were prepared in the report, including:

- Traffic Counts
- Bridges, Gates, Culverts
- Digital Raster Graphics
- Facilities
- Fire Locations
- Fire Perimeters
- Land Cover
- Material Sites
- Mining Claims

- Oil and Gas leases
- Parcel Boundaries
- Railroads
- Waterways
- Wells

Staff from Kenai Watershed Forum additionally included and prepared the following map layers:

- National Hydrography Dataset (USGS 2021b)
- Transportation Junctions
- Roads
- River miles of the main stem Kenai River and major tributaries

The above datasets were compiled into ArcGIS file geodatabases provided to ADEC on an external hard drive, and contain potentially relevant information about heavy metal nonpoint pollution sources. Each geodatabase's download metadata was recorded in an Excel spreadsheet table identifying a link, date of creation, type of potential pollution source, and if the source covers the entire study area. Original datasets were maintained in their native extent in order to encompass all tributaries transporting water into the Kenai River main stem.

Geospatial data gaps were also identified in the Robertson et al. 2020 report, and included the following:

- Impervious surfaces
- Galvanized metal surfaces
- Natural mineral deposits
- Snow storage locations
- Storm water drainage systems

Additional geospatial data gaps suggested by Kenai Watershed Forum staff include:

- Results from boat count surveys
- Fish habitat information

DISCUSSION

Copper and zinc sampling

Copper

No confirmed copper exceedances of hardness-dependent toxicity criteria were observed throughout the 2019-2020 sampling events. The most elevated copper value (8.16 ug/L) was observed on July 24, 2019 in the Kenai River mainstem at the Slikok Creek confluence and was above the chronic concentration criteria (CCC) of 4.55 ug/L (Table 4). Due to the proximity of potential anthropogenic sources in Slikok Creek, this observation suggests that further monitoring is warranted, including longitudinal survey(s) along with examination of potential point sources. However because the calcium and magnesium data used to generate the CCC value is asynchronous from the copper/zinc sampling event (Table 3) the

exceedance is not considered confirmed.

Other elevated copper samples include those from Upper No Name creek and Lower Beaver Creek during spring 2019, possibly the product of the rapid flush of nutrients and sediment associated with the spring snow melt freshet (USGS 2019). Other elevated copper samples were also observed at the City of Kenai Docks sites on July 24, 2019 and July 21, 2020. While diagnosing specific source locations of copper was not part of this analysis, creosote pilings such as those sometimes used in dock construction are known sources of copper (EPA 2015).

Zinc

Zinc exceedances of hardness-dependent CCC values were observed at several sampling locations in 2019-2020, including six of nine tributary sites and five of ten mainstem sites. Zinc exceedances suggested a spatial trend. Exceedances were observed primarily in the lower and estuary sections of the Kenai River (river mile 0 to 23, Figure 1), the segment of river that flows through the highest concentration of development within the Kenai River watershed, while no exceedances were observed at Jim's Landing, Skilak Lake Outlet, or Lower Funny River, sites which have minimal potential for anthropogenic influence.

The sampling event on April 30, 2019, where zinc exceedances were simultaneously observed at three tributary and five main stem sites (Figures 5, 6, and 7), could suggest a region-wide meteorological process such as snowmelt or precipitation that helps to drive the elevated concentrations and warrants further investigation.

Variation among replicate samples

The project QAPP (ADEC 2020a) requires data verification by examining variation among replicate samples compared to the designated samples and calculating the relative percent difference. In 2019-2020, outcomes revealed that data from some instantaneous grab samples do not meet data quality objectives defined for this project ($< 20\%$ RPD) and should not yet be employed to make management decisions. The average difference between replicates for both copper and zinc was in the range of $\pm 35\%$ (Table 5). In two of the fifteen replicate zinc values (Lower Slikok Creek April 30, 2019 and Upper Slikok Creek May 20, 2020), one replicate was above the zinc CCC threshold while the other was below (Figure 6).

The issue of sample precision could be addressed with several approaches, some which would involve modifying field and lab protocol and others that would not. One suggestion is to interpret and present CCC thresholds in future analyses in such a way that accounts for the inherent variation of instantaneous grab samples, assigning an error range to each copper and zinc result based on all replicate data available from 2000 – 2020. Current ADEC water quality criteria for copper and zinc do not incorporate error ranges into interpretation of sample values, thus this suggestion would involve modifying regulatory language. Additionally or alternatively, future field efforts may modify field and lab protocol to increase accuracy and precision. Further literature review of how other similar agencies and institutions nationwide have addressed this issue and consultation with other local experts may yield additional solutions and resulting modifications to the quality assurance plan.

Potential drivers of copper and zinc exceedances

Some examination of trends in metals concentrations in the Kenai River watershed (Guerron Orejuela 2016) and their probable sources (Sires 2017a) has been previously conducted, revealing more frequent

exceedances in the lower river section relative to the middle and upper sections. However, a conclusive analysis of which factors drive likelihood of toxicity criteria exceedance has yet to be performed. Such an analysis could leverage the uniquely robust twenty-year biannual Kenai River Baseline Water Quality Monitoring data set available through the Water Quality Portal (EPA 2021), along with other detailed meteorological, geographical, and biological data available for the region (EPSCoR 2020).

A variety of geographical as well as hydrological factors drive likelihood of water to exceed metals toxicity criteria. Geographical factors may include characteristics such as watershed size, percent of watershed impermeable area, watershed slope, local geological characteristics, quantity of upstream point sources, presence of manmade storm water drainage conveyance structures, and others. Hydrological factors may include precipitation pattern prior to sample date, stream flow volume, annual winter precipitation, and velocity of spring melt conditions. If conducted, results of a multivariate regression approach to conclusively identify predictors of exceedances could allow conservation-minded land owners and managers to most effectively identify locations and/or time periods where mitigation actions will be most effective. Once specific drivers of metals exceedances are identified, managers could work with members of area partnerships to develop site-specific mitigation plans involving strategic solutions such as phytoremediation tactics, riparian restoration efforts, strategic development, wetland preservation, and watershed user and landowner education (Liptan and Santen 2017).

Some drivers of exceedances are suggested for 2019-2020 data without the more detailed approach previously discussed. For example, the annual spring melt event (USGS 2019) likely represents an important driver of timing of elevated metals concentrations in spring (e.g. Figure 7), because the meltwater contains months of particulate accumulation collected throughout the winter months (Gouin et al. 2010; Blecken et al. 2012). Additionally, a period of precipitation following a long drought in summer may also be a driver of spikes in metals concentrations, as accumulated particles are flushed into the watershed (Prestes et al. 2006; Lau et al. 2009; Schiff and Tiefenthaler 2011).

Research recommendations

The results described in this work highlights the strengths and limitations of how instantaneous grab sample data may be applied towards understanding water quality in broader extents of space and time in the Kenai River watershed. Along with other efforts to synthesize and apply the region's long-term water quality data (Guerron Orejuela 2017), the results support growing evidence of elevated dissolved zinc and copper levels in limited parts of the lower Kenai River watershed region. While the specific factors most responsible for these elevated levels have yet to be fully elucidated, the present study indicates the need for proactive solutions directed towards a.) sampling methodology and interpretation, and b.) applying spatially explicit data to help choose where storm water infrastructure improvements will be most valuable.

Sampling Methodology

As described in the results section, the mean percent difference between replicate samples did not meet data quality objectives in the project's quality assurance plan, indicating a need to investigate ways to ensure that sampling protocols can satisfy data quality objectives in the future. A suggested course of action to address this issue could include a.) reviewing all available KRBWQM replicate sample data from year 2000 – present for spatial and temporal patterns in level of replicate sample variation, and b.) performing a literature review to examine successful methods of how this issue has been addressed in other research and monitoring programs.

One additional aspect of the exceedances observed in this study that the current dataset is unable to

address is the temporal duration of identified exceedances. It is unclear if the grab samples measured during typical sampling procedures represent concentrations that persist for hours, days, or weeks. In order to identify the typical duration of exceedances in watersheds where they are known to occur, it is advisable that metals are monitored throughout an expanded one-year period on a more frequent basis. For example, weekly or bi-weekly monitoring at select sites in the lower watershed region could help to pinpoint temporal drivers of exceedances. The most appropriate site for this expanded monitoring could be identified as those sites which have seen most frequent exceedances throughout the duration of monitoring from 2000 – present.

Applying new field sampling techniques could also offer improvements in data quantity, quality, and project cost. For example, some recent evidence indicates conductance (total dissolved ions), which may be continuously monitored with sondes (e.g. Hydrolab), might serve as a proxy for metals concentrations (Morel et al. 2020). A field sampling program employing both traditional grab samples and continuously deployed sondes could provide insight as to which method is most economical and appropriate for long term monitoring efforts.

Finally, new knowledge of the characteristics and effects of urban runoff pollution on freshwater aquatic communities are continuously being discovered (Tian et al. 2020), thus regular assessment of water quality monitoring priorities based on updated knowledge is critical.

Applying Data to Prioritize Potential Sites for Storm water Infrastructure Improvement

Examination of the long-term Kenai River water quality dataset (2000 – present), as recommended in recent Alaska Department of Environmental Conservation strategy documents (ADEC 2020b) (section 2.4), could reveal if the trends in rising zinc and copper levels at some sites identified from 2010 – 2014 (Guerron Orejuela 2016; Sires 2017b) have changed since the trend was identified. Additionally, a variety of storm water interventions have been applied throughout the lower Kenai River basin to reduce the impact of urban runoff, including sedimentation basins, diffuser outfalls, and rain gardens (City of Soldotna 2016). An examination of the location(s) and installation dates of these interventions and downstream water quality might help reveal if they have been effective in reducing pollutant concentrations.

Should an examination of the full temporal extent of copper and zinc data indicate continuing exceedances, the need grows to prioritize locations for potential interventions for both source reduction and runoff mitigation. One approach for this procedure could include a GIS mapping exercise employing both the water quality and geospatial data products described in this report. Generally, this work would consist of 1.) addressing data gaps identified in the mapping results section and 2.) once data gaps are addressed, applying all appropriate geospatial and water quality data towards a spatially explicit model that identifies likelihood of toxicity exceedance within individual HUC12 units (smallest mapped sub-watershed size) in the Lower Kenai River region. At a basic level, a map visualization with HUC 12 units color-coded to indicate numerical count of the total number of potential sources within each could offer a rough visualization of how density of potential sources varies across the landscape. A visual examination of how the pattern of these sources relates to observed trends in zinc and copper from 2000 - present may reveal general areas most appropriate for potential interventions. A more complex approach could include applying an existing watershed model such as SPARROW (SPAtially Referenced Regression On Watershed attributes) (USGS 2021a) to interpolate spatially limited water quality data over a broad geographical area. The intended output of this or another similar model would incorporate geographical and hydrological factors that can affect contaminant loadings, and offer a substantially more robust prioritization tool. After identifying the most relevant sub-watersheds for potential interventions, economic and logistical considerations would ultimately determine which projects are initially feasible.

Addressing the identified geospatial data gaps would require varying levels of effort for each type. For example, creation of an impervious surfaces layer would involve substantial efforts in heads-up digitizing and ground-truthing fieldwork of impervious surfaces, while including a stormwater facilities map may involve merely digitizing existing data (City of Soldotna 2016) to a geodatabase format. Additionally, if the geospatial products described in this report prove useful in identifying potential pollutant sources, it is recommended that they be updated every five to ten years to account for development and landscape change (EPSCoR 2016). Regarding the photos shapefile of potential sources on the main stem Kenai River generated in this project, use of satellite or drone imagery is a potential avenue for acquiring future images against which to compare past observations.

CONCLUSION

This document is intended as a draft report addressing the findings from compiled copper and zinc data gathered during April, May, and July sampling events in 2019-2020. While the data collected throughout this study will provide further insight into the current sources and levels of copper and zinc throughout the Kenai River watershed, much of the temporal variation and point sources of these heavy metals remains to be characterized. As a result, the following preliminary study expansions are advised:

- 1. Perform a basic exploratory data analysis to summarize all available water quality data from 2000 – 2020 and apply results**
 - a. Ensure all data 2000 - present is archived and available for public access through the EPA water quality portal (Meyer 2021a).
 - b. Examine site-specific trends from 2000 – 2020 to identify spatial and temporal predictors of copper and zinc exceedance
 - c. Using the identified predictors, choose a subset of watersheds where mitigation actions may be potentially feasible and appropriate
 - d. Implement restoration and other mitigation efforts in tandem with local partnerships
- 2. Expand copper and zinc sampling study through increased sampling of Kenai River mainstem and tributary sites**
 - a. Assess fluctuations in copper and zinc levels over the period of one year, particularly at sites that saw exceedances:
 - i. Tributaries: No Name Creek, Beaver Creek, Slikok Creek, Soldotna Creek
 - ii. Mainstem: from Cunningham Park (RM 6.5) to Swiftwater Park (RM 23)
 - b. Expand sampling efforts along longitudinal transects in tributaries experiencing exceedances in order to identify areas of concern within each tributary
 - c. Perform opportunistic sampling at known and suspected discrete sources before, during, and after select precipitation and melt events, at locations that may include storm water outfalls, road crossings, and outlets draining large impervious surfaces.
 - d. Perform literature review on the topics of sample precision, monitoring for predicted effects of runoff pollution on aquatic organisms, and bioaccumulation of copper and zinc in salmonids and other fishes.
- 3. Track changes in development throughout the Kenai River watershed to address anthropogenic impact over time**
 - a. Conduct Kenai River photography trips every 5-10 years
 - b. Monitor new development over time in order to conduct annual updates of mapping tool
- 4. Expand awareness of educational programs for local landowners and watershed user groups including topics such as responsible river use and effective property restoration projects**

The Kenai River watershed boasts one of the longest term water quality datasets in the state of Alaska;

an invaluable resource showing varying levels of copper and zinc that warrant further investigation in order to apply effective solutions.

From information to action

As stream-adjacent development and subsequent development pressures increase along the Kenai River mainstem and its tributaries (Schoen et al. 2017), study expansion remains a critical step that would lead to effective, strategic mitigation efforts throughout this highly-revered watershed. However, the knowledge gained from the study expansion will have utility only if successful, feasible mitigation strategies can also be demonstrated.

A pilot project to install proven green infrastructure that filters many pollutants of concern would be a substantive step towards more widespread community adoption. Visible, proven success stories will encourage land managers and property owners to adopt green infrastructure practices both in mitigation actions and in new designs (City of Homer 2020). Such actions are in alignment with goals outlined in section 4.1 in the City of Soldotna 2015 Soldotna Drainage Master Plan:

“Use public facility development and operations to model sustainable design techniques, such as using green areas along roads for stormwater detention and treatment, maximizing retention of native vegetation, reducing the impermeable footprint of new development...” (City of Soldotna 2016).

Specifically, opportunistic monitoring could be performed below known sources or sources of untreated storm water outfall (ADEC, 2011) before, during, and after installation of mitigating infrastructure such as sedimentation basins, diffuser outfalls, rain gardens, bio-swales, or stream bank revegetation. While the study expansions described will help better define the most ecologically significant metals pollution exceedances, even prior to having its results and conclusions, streams may be targeted for mitigation wherever cooperative landowners are willing.

DATA AVAILABILITY

All data and analysis used to generate this report is available at https://github.com/Kenai-Watershed-Forum/KWF_Metals_2019_2020.

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APPENDIX A: FIGURES

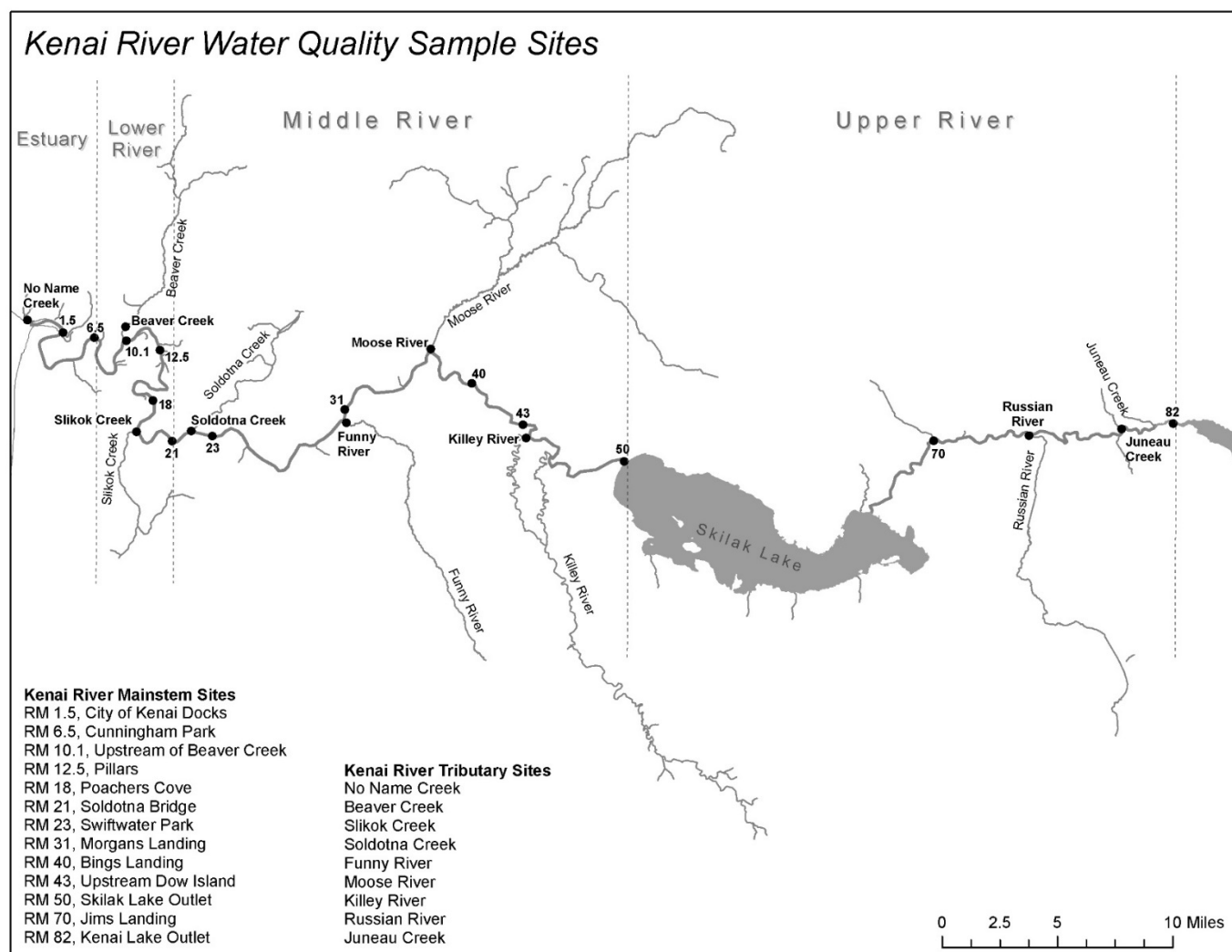


FIGURE 1. DIVISION OF THE KENAI RIVER WATERSHED (LOWER, MIDDLE, AND UPPER KENAI RIVER) AND WATER QUALITY MONITORING SITE LOCATIONS DURING BIANNUAL (2000 – PRESENT) KRBWQM SAMPLING EVENTS.



Site ID	Site Name
1	City of Kenai Docks
2	Cunningham Park
3	Jim's Landing
4	Lower Beaver Creek
5	Lower Funny River
6	Lower No Name Creek
7	Lower Slikok Creek
8	Lower Soldotna Creek
9	Pillars
10	Poachers Cove
11	Skilak Lake Outlet
12*	Slikok Confluence
13	Soldotna Bridge
14	Swiftwater Park
15*	Upper Beaver Creek
16*	Upper No Name Creek
17*	Upper Slikok Creek
18*	Upper Soldotna Creek
19*	Upstream of Beaver Creek

FIGURE 2. 2019 - 2020 SAMPLING LOCATIONS. SITES THAT ARE NEWLY INCLUDED IN 2019 – 2020 FIELD SAMPLING ARE NOTED WITH AN ASTERISK (*). POINTS 7 (LOWER SLIKOK CREEK) AND 12 (SLIKOK CONFLUENCE) ARE SUPERIMPOSED AT THIS MAP SCALE.

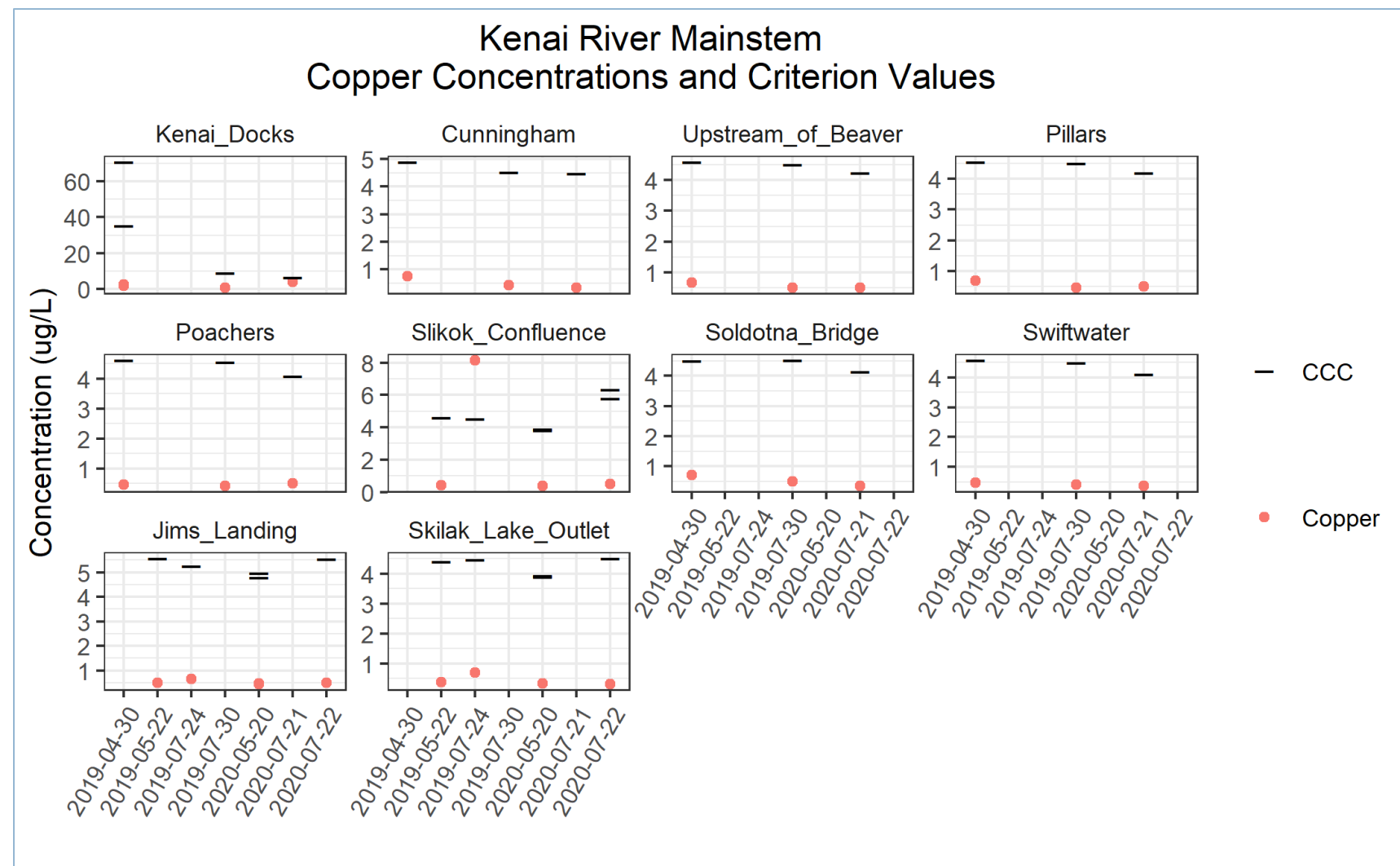


FIGURE 3. 2019-2020 KENAI RIVER MAINSTEM SITES COPPER CONCENTRATIONS AND CRITERION (CCC) VALUES.

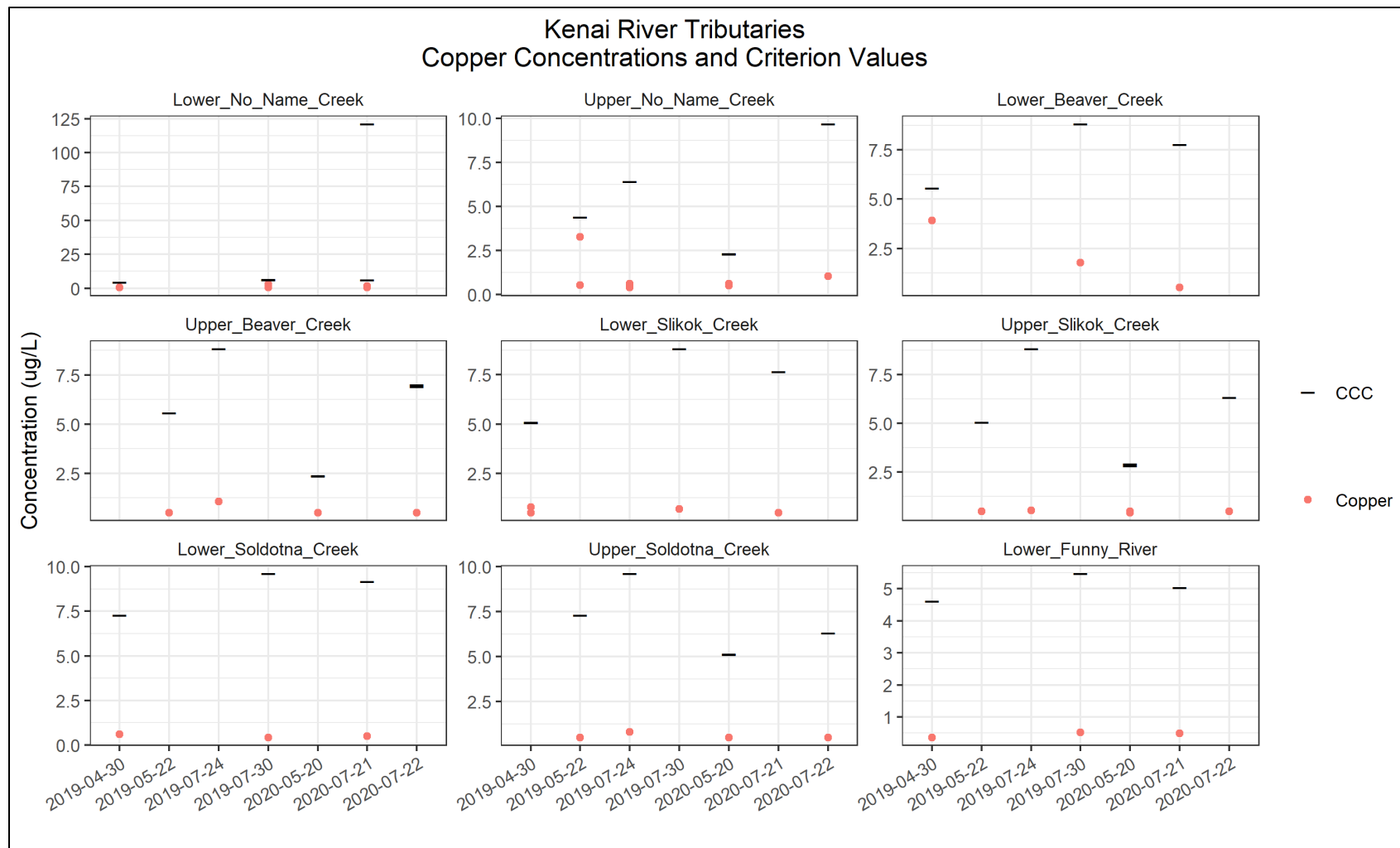


FIGURE 4. 2019-2020 KENAI RIVER TRIBUTARY SITES COPPER CONCENTRATIONS AND CRITERION (CCC) VALUES.

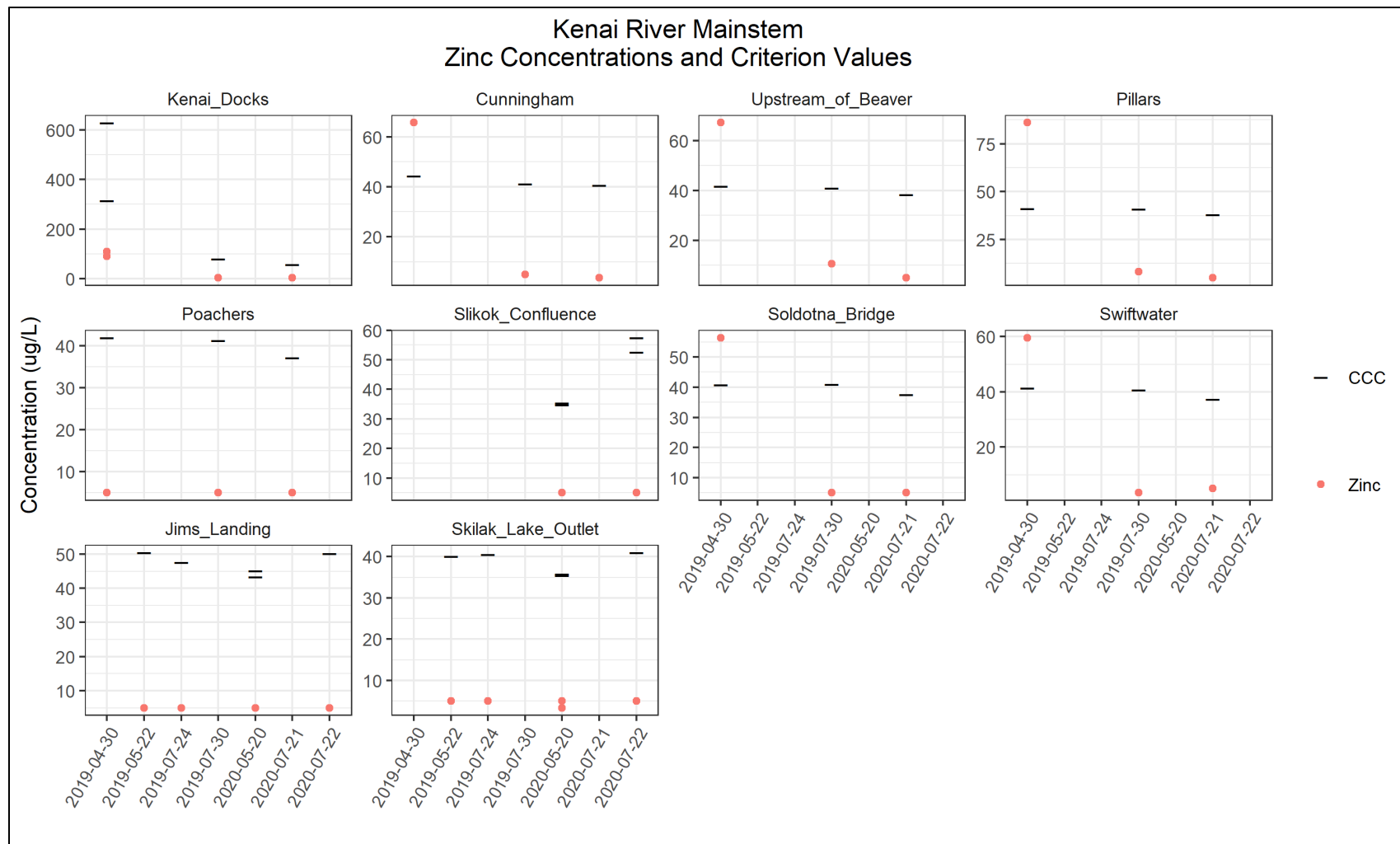


FIGURE 5. KENAI RIVER MAINSTEM SITES ZINC CONCENTRATIONS AND CRITERION (CCC) VALUES.

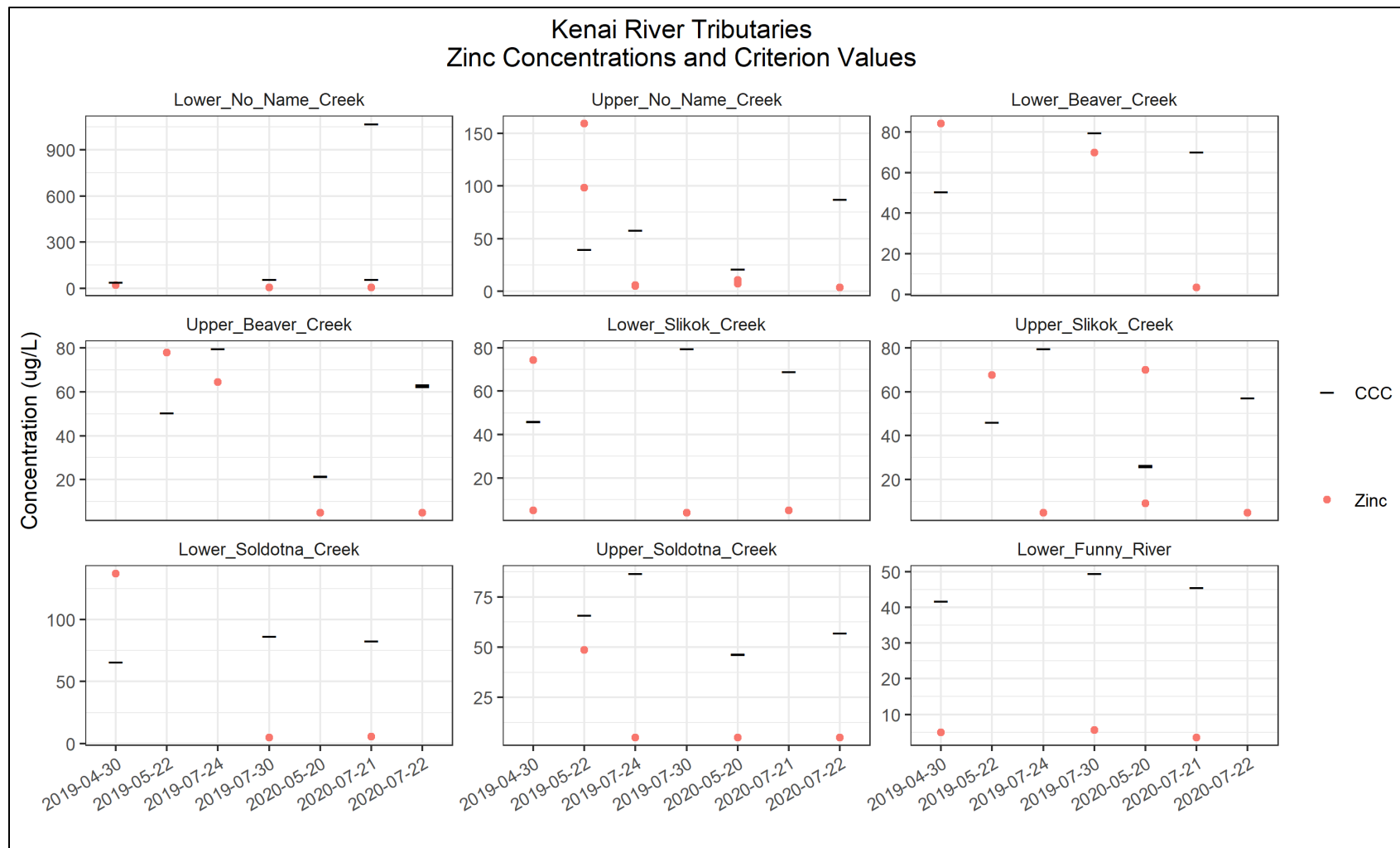


FIGURE 6. KENAI RIVER TRIBUTARY SITES ZINC CONCENTRATIONS AND CRITERION (CCC) VALUES.

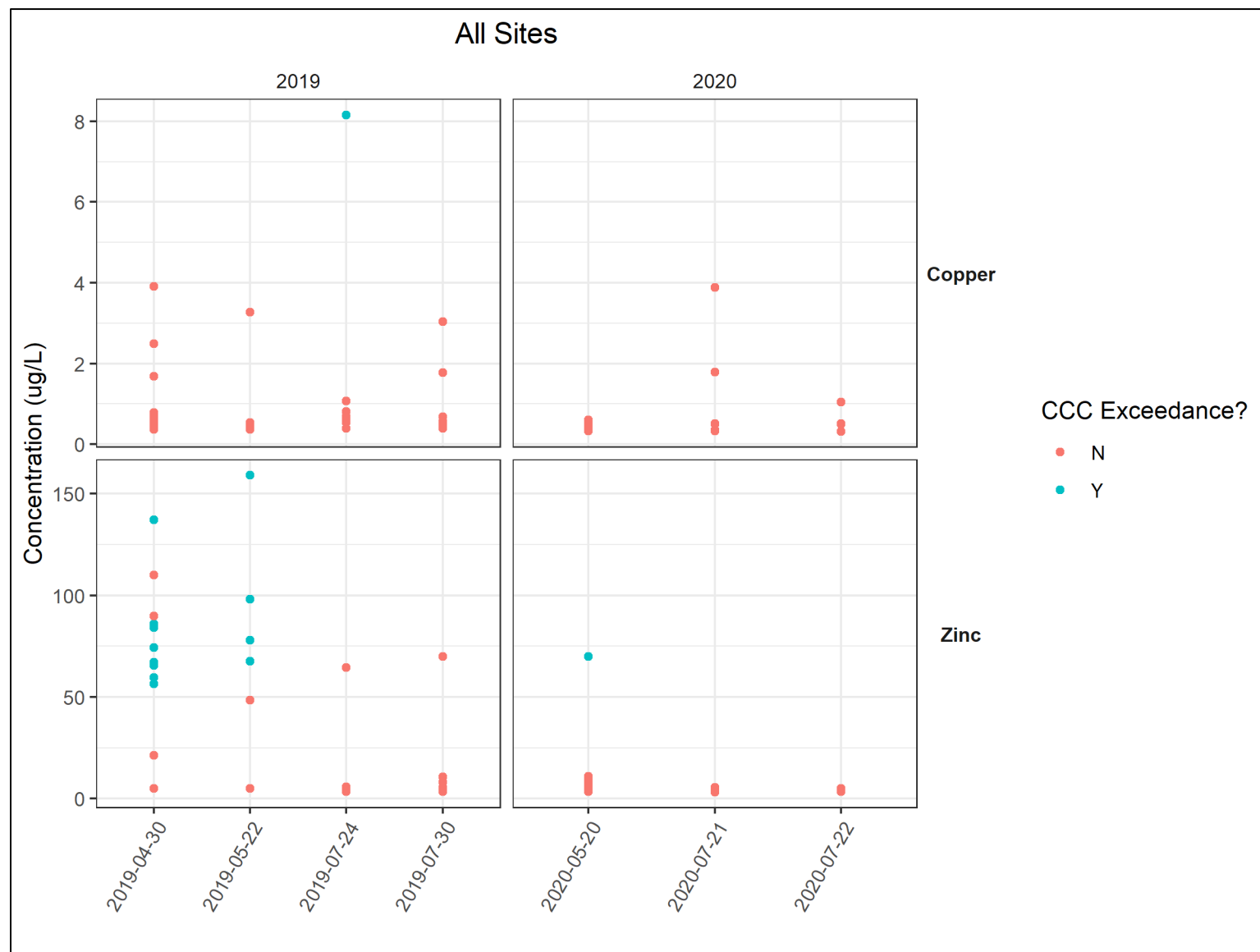


FIGURE 7. KENAI RIVER MAINSTEM AND TRIBUTARIES, DISSOLVED COPPER AND ZINC SAMPLE RESULTS BY YEAR, 2019 – 2020. COLOR DESIGNATES EXCEEDANCE OF CRITERION (CCC) VALUES.

APPENDIX B: TABLES

TABLE 1. ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION WATER QUALITY STANDARDS AND PERTAINING CALCULATIONS. (CCC = CRITERION CHRONIC CONCENTRATION).

Parameter	ADEC Standard	Reference
Copper	$CCC = (e^{0.8545(\ln \text{hardness}^*) - 1.702}) * 0.96$ for aquatic life, fresh water, and chronic exposure.	ADEC. (2008). Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances.
Zinc	$CCC = (e^{0.8473(\ln \text{hardness}^*) + 0.884}) * 0.986$ for aquatic life, fresh water, and chronic exposure.	ADEC. (2008). Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances.
Hardness*	$\text{Hardness} = 2.497(\text{Ca mg/L}) + 4.119(\text{Mg mg/L})$	Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (Eds.). 1998. Standard Methods for the Examination of Water and Wastewater (20th ed.), Washington D.C. American Public Health Association, American Water Works Association, and Water Environment Federation.

TABLE 2. SAMPLING SITE COORDINATES.

Site	Habitat	Latitude	Longitude
Lower No Name Creek	Tributary	60.550888	-151.26842
Upper No Name Creek	Tributary	60.577846	-151.26859
Lower Soldotna Creek	Tributary	60.483364	-151.05766
Upper Soldotna Creek	Tributary	60.550828	-150.95833
Lower Beaver Creek	Tributary	60.548029	-151.14324
Upper Beaver Creek	Tributary	60.641201	-151.08472
Lower Slikok Creek	Tributary	60.482318	-151.12705
Upper Slikok Creek	Tributary	60.402664	-151.14739
Lower Funny River	Tributary	60.489963	-150.86098
City of Kenai Docks	Mainstem	60.54368	-151.22294
Cunningham Park	Mainstem	60.54081	-151.18278
Upstream of Beaver Creek	Mainstem	60.539279	-151.14226
Pillars	Mainstem	60.533743	-151.09926
Poacher's Cove	Mainstem	60.502005	-151.10697
Soldotna Bridge	Mainstem	60.476634	-151.0821
Slikok Creek Kenai River Confluence	Mainstem	60.482752	-151.12512
Swiftwater Park	Mainstem	60.480338	-151.03085
Jim's Landing	Mainstem	60.481392	-150.11502
Skilak Lake Outlet	Mainstem	60.467517	-150.50779

TABLE 3. INSTANCES WHERE ZINC AND COPPER DATA DIFFERS FROM PAIRED CALCIUM AND MAGNESIUM DATA.

Copper/Zinc Sample Date	Copper/Zinc Sample Location	Calcium/Magnesium Sample Date	Calcium/Magnesium Sample Location
May 22, 2019	Upper No Name Creek	April 30, 2019	Lower No Name Creek
May 22, 2019	Upper Beaver Creek	April 30, 2019	Lower Beaver Creek
May 22, 2019	Upper Slikok Creek	April 30, 2019	Lower Slikok Creek
May 22, 2019	Upper Soldotna Creek	April 30, 2019	Lower Soldotna Creek
May 22, 2019	Slikok Creek – Kenai River Confluence	April 30, 2019	Poacher’s Cove
July 30, 2019	Upper No Name Creek	July 24, 2019	Upper No Name Creek
July 30, 2019	Upper Beaver Creek	July 24, 2019	Upper Beaver Creek
July 30, 2019	Upper Slikok Creek	July 24, 2019	Upper Slikok Creek
July 30, 2019	Upper Soldotna Creek	July 24, 2019	Upper Soldotna Creek
July 30, 2019	Slikok Creek – Kenai River Confluence	July 24, 2019	Poacher’s Cove

TABLE 4. (PAGE 1 OF 3) COPPER AND ZINC LEVELS AND HARDNESS-DEPENDENT CRITERION STANDARDS.

					Copper		Zinc	
Site name	River mile	Date	Location on Kenai River	Hardness (mg/L)	Result (ug/L)	Standard: CCC (ug/L)	Result (ug/L)	Standard: CCC (ug/L)
Lower No Name Creek		4/30/2019	Tributary	32.59	0.668 J	4.40	21.3	39.92
		7/30/2019	Tributary	51.22	0.451 J	6.48	5.53 J	58.56
		7/21/2020	Tributary	49.86	0.5 U	6.33	5 U	57.24
Upper No Name Creek		5/22/2019	Tributary	32.59	0.53 J	4.40	98.1	39.92
		7/24/2019	Tributary	50.85	0.39 J	6.44	5.12 J	58.20
		5/20/2020	Tributary	15.58	0.606 J	2.34	10.9	21.36
		7/22/2020	Tributary	82.32	1.04	9.71	3.46 J	87.53
Lower Beaver Creek		4/30/2019	Tributary	43.06	3.91	5.58	84.1	50.55
		7/30/2019	Tributary	73.65	1.77	8.83	69.9	79.66
		7/21/2020	Tributary	63.36	0.509 J	7.77	3.27 J	70.12
Upper Beaver Creek		5/22/2019	Tributary	43.06	0.5 U	5.58	77.80	50.55
		7/24/2019	Tributary	73.65	1.07	8.83	64.40	79.66
		5/20/2020	Tributary	15.7	0.5 U	2.36	5 U	21.5
		7/22/2020	Tributary	56.16	0.5 U	7.01	5 U	63.31
Lower Slikok Creek		4/30/2019	Tributary	38.45	0.783 J	5.07	74.4	45.93
		7/30/2019	Tributary	73.58	0.684 J	8.83	4.01 J	79.60
		7/21/2020	Tributary	62.29	0.5 J	7.66	5 U	69.12
Upper Slikok Creek		5/22/2019	Tributary	38.45	0.5 U	5.07	67.60	46.22
		7/24/2019	Tributary	73.58	0.53 J	8.83	5U	79.60
		5/20/2020	Tributary	20.19	0.431 J	2.92	69.9	26.61
		7/22/2020	Tributary	49.82	0.5 U	6.33	5 U	57.20
Lower Soldotna Creek		4/30/2019	Tributary	58.94	0.597 J	7.30	137	65.96
		7/30/2019	Tributary	81.39	0.424 J	9.62	5 U	86.70
		7/21/2020	Tributary	77.10	0.5 U	9.19	5.52 J	82.81
Upper Soldotna Creek		5/22/2019	Tributary	58.94	0.5 U	7.30	48.50	65.96
		7/24/2019	Tributary	81.39	0.81 J	9.62	5U	86.70
		5/20/2020	Tributary	38.91	0.5 U	5.12	5 U	46.39
		7/22/2020	Tributary	49.78	0.5 U	6.32	5 U	57.16
Copper, zinc exceedances based on water quality criteria for aquatic life for fresh water (chronic exposure) established by Alaska Department of Environmental Conservation								
CCC = criterion chronic concentration (freshwater) () = duplicate sample J = quantitation is an estimate U = analyzed but not detected Values in parentheses are duplicate samples								

TABLE 4 (PAGE 2 OF 3). COPPER AND ZINC LEVELS AND HARDNESS-DEPENDENT STANDARDS FOR SAMPLING EVENTS ON THE KENAI RIVER MAINSTEM AND TRIBUTARIES.

					Copper		Zinc	
Site name	River mile	Date	Location on Kenai River	Hardness (mg/L)	Result (ug/L)	Standard: CCC (ug/L)	Result (ug/L)	Standard: CCC (ug/L)
Lower Funny River		4/30/2019	Tributary	34.41	0.363 J	4.61	5 U	41.80
		7/30/2019	Tributary	42.01	0.514 J	5.47	5.63 J	49.50
		7/21/2020	Tributary	38.13	0.495 J	5.03	3.53 J	45.60
City of Kenai Docks	1.5	4/30/2019	Mainstem	842.68	2.49	70.9	89.9	628.18
		7/30/2019	Mainstem	74.98	0.562 J	8.97	5 U	80.87
		7/21/2020	Mainstem	50.23	3.88	6.37	4.16 J	57.60
Cunningham Park	6.5	4/30/2019	Mainstem	36.84	0.751 J	4.89	65.6	44.29
		7/30/2019	Mainstem	33.74	0.428 J	4.53	5 U	41.12
		7/21/2020	Mainstem	33.23	0.334 J	4.47	3.59 J	40.58
Upstream of Beaver Creek	10.1	4/30/2019	Mainstem	34.23	0.66 J	4.59	67.1	41.62
		7/30/2019	Mainstem	33.62	0.497 J	4.52	10.7	40.99
		7/21/2020	Mainstem	31.16	0.5 U	4.24	5 U	38.43
Pillars	12.5	4/30/2019	Mainstem	33.90	0.681 J	4.55	86	41.28
		7/30/2019	Mainstem	33.58	0.452 J	4.52	8.14 J	40.94
		7/21/2020	Mainstem	30.83	0.5 U	4.20	5 U	38.08
Poachers Cove	18	4/30/2019	Mainstem	34.53	0.47 J	4.62	5 U	41.92
		7/30/2019	Mainstem	33.87	0.42 J	4.55	5 U	41.25
		7/21/2020	Mainstem	29.96	0.5 U	4.10	5 U	37.17
Slikok Creek-Kenai River Confluence	19.00	5/22/2019	Mainstem	34.53	0.42 J	4.62	5U	41.92
		7/24/2019	Mainstem	34.87	8.16	4.55	3.55 J	41.25
		5/20/2020	Mainstem	28.31	0.387 J	3.9	5 U	35.43
		7/22/2020	Mainstem	50.1	0.515 J	6.36	5 U	57.47
Soldotna Bridge	21	4/30/2019	Mainstem	33.49	0.716 J	4.50	56.4	40.85
		7/30/2019	Mainstem	33.58	0.493 J	4.52	5 U	40.94
		7/21/2020	Mainstem	30.33	0.348 J	4.14	5 U	37.57
Swiftwater Park	23	4/30/2019	Mainstem	34.11	0.462 J	4.58	59.6	41.49
		7/30/2019	Mainstem	33.33	0.398 J	4.49	3.49 J	40.69
		7/21/2020	Mainstem	30.08	0.359 J	4.11	5 U	37.30
Copper, zinc exceedances based on water quality criteria for aquatic life for fresh water (chronic exposure) established by Alaska Department of Environmental Conservation								
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TABLE 4 (PAGE 3 OF 3). COPPER AND ZINC LEVELS AND HARDNESS-DEPENDENT STANDARDS FOR SAMPLING EVENTS ON THE KENAI RIVER MAINSTEM AND TRIBUTARIES.

					Copper		Zinc	
Site name	River mile	Date	Location on Kenai River	Hardness (mg/L)	Result (ug/L)	Standard: CCC (ug/L)	Result (ug/L)	Standard: CCC (ug/L)
Skilak Lake Outlet	50.00	5/22/2019	Mainstem	32.72	0.37 J	4.42	5U	40.06
		7/24/2019	Mainstem	33.20	0.70	4.47	5U	40.56
		5/20/2020	Mainstem	28.68	0.341 J	3.95	3.41 J	35.83
		7/22/2020	Mainstem	33.59	0.313 J	4.52	5 U	40.95
Jim's Landing	70.00	5/22/2019	Mainstem	42.94	0.5 U	5.57	5U	50.43
		7/24/2019	Mainstem	40.07	0.64	5.25	5U	47.56
		5/20/2020	Mainstem	37.7	0.472 J	4.98	5 U	45.16
		7/22/2020	Mainstem	42.77	0.496 J	5.55	5 U	50.26
Copper, zinc exceedances based on water quality criteria for aquatic life for fresh water (chronic exposure) established by Alaska Department of Environmental Conservation								
CCC = criterion chronic concentration (freshwater) () = duplicate sample J = quantitation is an estimate U = analyzed but not detected Values in parentheses are duplicate samples								

TABLE 5. RELATIVE DIFFERENCE LEVELS (RPD) OF DUPLICATE SAMPLES BY SITE AND DATE.

River Mile*	Site	Date	Parameter	RPD (%)	>20%
Trib	Lower_No_Name_Creek	7/30/2019	Copper	148.32%	Y
Trib	Lower_No_Name_Creek	7/21/2020	Copper	112.66%	Y
1.5	City_of_Kenai_Docks	4/30/2019	Copper	38.85%	Y
19	Lower_Slikok_Creek	4/30/2019	Copper	44.12%	Y
19	Slikok_Creek_Kenai_River_Confluence	5/20/2020	Copper	3.95%	
19	Slikok_Creek_Kenai_River_Confluence	7/22/2020	Copper	2.96%	
50	Skilak_Lake_Outlet	5/20/2020	Copper	4.19%	
70	Jims_Landing	5/20/2020	Copper	5.44%	
Trib	Upper_No_Name_Creek	5/22/2019	Copper	144.21%	Y
Trib	Upper_No_Name_Creek	7/24/2019	Copper	44.00%	Y
Trib	Upper_Beaver_Creek	5/20/2020	Copper	0.00%	
Trib	Upper_No_Name_Creek	5/20/2020	Copper	19.76%	
Trib	Upper_Slikok_Creek	5/20/2020	Copper	14.82%	
Trib	Upper_Soldotna_Creek	5/20/2020	Copper	0.00%	
Trib	Upper_Beaver_Creek	7/22/2020	Copper	0.00%	
Trib	Lower_No_Name_Creek	7/30/2019	Zinc	4.06%	
Trib	Lower_No_Name_Creek	7/21/2020	Zinc	28.57%	Y
1.5	City_of_Kenai_Docks	4/30/2019	Zinc	20.11%	Y
19	Lower_Slikok_Creek	4/30/2019	Zinc	174.81%	Y
19	Slikok_Creek_Kenai_River_Confluence	5/20/2020	Zinc	0.00%	
19	Slikok_Creek_Kenai_River_Confluence	7/22/2020	Zinc	0.00%	
50	Skilak_Lake_Outlet	5/20/2020	Zinc	37.81%	
70	Jims_Landing	5/20/2020	Zinc	0.00%	
Trib	Upper_No_Name_Creek	5/22/2019	Zinc	47.37%	
Trib	Upper_No_Name_Creek	7/24/2019	Zinc	11.94%	
Trib	Upper_Beaver_Creek	5/20/2020	Zinc	0.00%	
Trib	Upper_No_Name_Creek	5/20/2020	Zinc	42.90%	Y
Trib	Upper_Slikok_Creek	5/20/2020	Zinc	153.97%	Y
Trib	Upper_Soldotna_Creek	5/20/2020	Zinc	0.00%	
Trib	Upper_Beaver_Creek	7/22/2020	Zinc	0.00%	

Overall mean difference (mean \pm standard error):

- Copper: $38.9 \pm 13.6\%$
- Zinc : $34.8 \pm 14.3\%$

* Refers to river mile of the main stem Kenai River