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 QAPP[1], 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

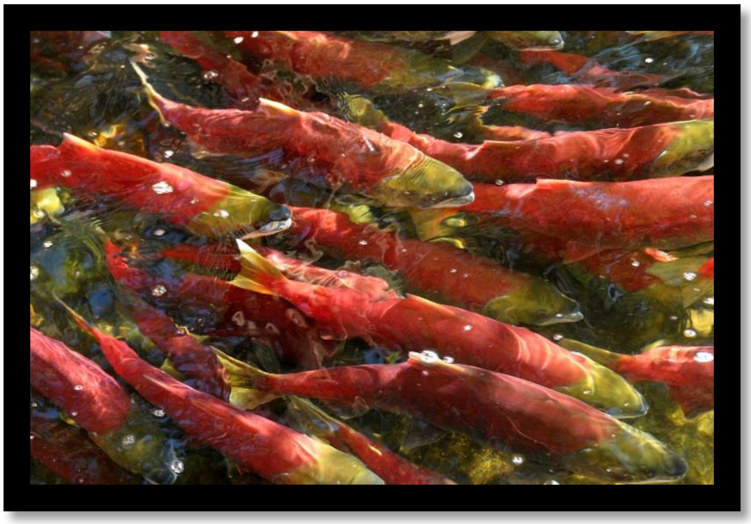
ADEC. 2021 Kenai River Water Quality Monitoring. Prepared by S. Apsens and J. Petitt. Alaska Department of Environmental Conservation, Division of Water, Soldotna, AK. 36 pg.

EPA. 1996. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency, Office of Water, Engineering and Analysis Division, Washington D.C. 39 pg.

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.

KWF. 2019. Quality Assurance Project Plan: Kenai River Watershed Monitoring Program. Version 2. Prepared for the State of Alaska, Department of Environmental Conservation, Division of Water. 70 pg.

2019 FIELD REPORT: COPPER AND ZINC LEVELS THROUGHOUT THE KENAI RIVER WATERSHED



2/26/2020

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Prepared by:
Maggie Harings
Environmental Scientist
Kenai Watershed Forum
(907) 260-5449 x1207
www.kenaiwatershed.org

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.

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PURPOSE

This field report serves as a draft under the Alaska Clean Water Actions (ACWA) grant 19-02, FAIN: 00J84604 for the Alaska Department of Environmental Conservation (ADEC). Its purpose is to highlight fieldwork and mapping efforts conducted in 2019 to assess levels of copper and zinc, as well as to their potential sources 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 (KWF, 2017). This field report will address the following questions:

1. How were copper and zinc sampling locations chosen and how was sampling conducted in 2019?

2. What were the copper and zinc levels at specific locations throughout the Kenai River watershed during spring and summer sampling events in 2019?

3. Where did copper and zinc exceedances occur throughout the Kenai River watershed in 2019 during spring and summer sampling events?

INTRODUCTION

The Kenai River is a glacially-fed system located on the Kenai Peninsula. This 82-mile river begins at the outlet of Kenai Lake and flows into a branch of the Gulf of Alaska commonly known as Cook Inlet. 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 Kenai). Several major, non-glacial tributaries flow into the Kenai River (Figure 1).

The Kenai River watershed plays host to hundreds of thousands of Pacific salmon that utilize its habitat for rearing and spawning. These salmon are intrinsic pieces of Alaskan economy, recreation, and culture. As a result, the Kenai River watershed is often targeted for conservation efforts, as it experiences significant anthropogenic pressures throughout the year. Over 20 years ago, the Kenai Watershed Forum (KWF) identified a need for monitoring several water quality parameters often influenced by development, impervious surfaces, boat use, etc… In response, KWF established the Kenai River Baseline Water Quality Monitoring (KRBWQM) program in 2000 to track water quality changes over time. Several sites were chosen along the Kenai River mainstem and in its major tributaries with the intention of providing information on overall watershed health twice per year (Figure 1). Included in water quality samples taken each year are copper, zinc, calcium, and magnesium. Freshwater exceedances of copper and zinc are identified when their levels are compared to hardness-dependent freshwater criteria continuous concentration (CCC) whose calculations requires the input of calcium and magnesium levels (Table 1; ADEC, 2008).

KRBWQM within the Kenai River watershed demonstrated a notable increase in dissolved copper and zinc concentrations from 2010 through 2014 as compared with previous sampling years (KWF, 2017). These heavy metals can have harmful effects on Pacific salmon and the watersheds they rely on. Elevated levels of copper can lead to toxic effects on a salmon's olfactory nervous system, which is critical for survival and migratory success (Baldwin et al, 2003). Chinook salmon (*Oncorhynchus tshawytscha*) have shown increased susceptibility to elevated zinc levels during early life stages-a critical period of time in development (Chapman, 1978).

These elevated levels of copper and zinc warranted further investigation and, through ACWA grant 19-02/FAIN: 00J84604, KWF identified four tributary and three mainstem sites throughout the Kenai River watershed for further testing in the spring and summer of 2019 and 2020 (Figure 2). Five river trips were also conducted in order to photograph all zinc and copper sources visible from the Kenai River. These photos were incorporated into a shapefile that was established to document other adjacent sources of these heavy metals including impervious surfaces, boat landings, and wastewater discharge. All sampling and mapping efforts are ongoing and will be completed in 2020 and will be further detailed in a final report.

METHODS

Copper and zinc sampling*

*Note: that 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 Tables 2-5.

Kenai River Baseline Water Quality Monitoring (KRBWQM)

KWF conducted biannual KRBWQM events in 2019. These were cooperative events that, in 2019, required the participation and/or financial contributions of several agencies and organizations including:

- Alaska Department of Fish and Game
- Cities of Kenai, 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

Water samples were taken from 14 mainstem sites on the Kenai River and eight tributary sites near their confluence with the Kenai River (Figure 1). These sites were originally chosen in order to accurately represent the Kenai River watershed's ambient water quality conditions (Ashton, 1998). Samples taken were analyzed for several parameters including zinc, copper, calcium, and magnesium. Samples were taken and analyzed at five tributaries and seven mainstem Kenai River sites in April, and four tributaries and seven mainstem Kenai River sites in July.

After a training session, sampling participants were split into small groups and sampled 2-5 sites by foot or boat on April 30, 2019 and July 30th, 2019. All samples were collected on the same day and the timing of sample collection coincided with an outgoing tide to reduce potential saltwater contamination of samples. Individuals collecting samples by foot waded into the water until the water depth was around two feet and the participant was offshore in flowing water. 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. While wearing clean gloves, samples were collected by facing upstream, removing the bottle seal, inverting the bottle and plunging it roughly 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 and shipped in insulated coolers with ice packs via Grant Aviation. They were retrieved and analyzed by SGS North American, Inc (Anchorage) within the holding time of each sample. 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 (KWF, 2019).

Results were reported digitally; data management was done so in Microsoft Excel. Hardness and hardness-dependent freshwater CCC criteria were calculated using equations included in the Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances publication, and can be found in Table 1.

Copper and zinc-specific sampling events

In addition to the KRBWQM sampling events, KWF staff and sampling volunteers conducted sampling for copper and zinc on May 22, 2019 and July 24, 2019 (Figure 2). Sample sites included four tributary and three mainstem Kenai River locations (Figure 2; Table 3; Table 5).

Tributary sites were selected based on their historically-elevated levels of copper and/or zinc as well as their location above most anthropogenic influence. The Slikok Creek confluence was chosen in order to compare the levels on copper and zinc found within the Slikok Creek tributary. Skilak Lake and Jim's Landing were chosen as they are located upstream of the majority of development along the Kenai river and would provide relative background data on zinc and copper. Uniquely, Jim's Landing is a designated, popular boat launch utilized by recreationists using drift-only boats. All sampling procedures aligned with the ADEC-approved 2019 QAPP and are discussed in further detail throughout the "Copper and zinc sampling: Kenai River Baseline Water Quality Monitoring (KRBWQM)" section of this document.

Results were reported digitally; data management was done so in Microsoft Excel. Hardness and hardness-dependent freshwater CCC criteria were calculated using equations included in the Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances publication, and can be found in Table 1.

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 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 (RL) 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.

Potential sources throughout the Kenai River watershed

Following the literature review conducted by KWF in 2017, potential sources of copper and zinc were identified throughout the Kenai River watershed. Copper sources 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 (KWF, 2017). Similarly, zinc sources included galvanized metals, tire wear, motor oil/hydraulic fluid, fertilizer/pesticides/fungicides, natural mineral depots, mining activity, forest fires, and brakes (KWF, 2017). Using these results from the literature review, KWF identified potential local producers of copper and zinc through a mapping exercise.

RESULTS

Copper and zinc sampling

Kenai River Baseline Water Quality Monitoring (KRBWQM)

Copper levels ranged from undetected to 3.91 µg/L at Beaver Creek during the April sampling event while the freshwater CCC criteria ranged from 4.4 µg/L at No Name Creek to 70.9 µg/L at Kenai City Docks (Table 2). Notably, the second highest freshwater CCC criterion calculated corresponded to the

Kenai City Docks (duplicate) sample, 35.43 µg/L (Table 2). While no exceedances occurred during the April sampling event, Beaver Creek did result in a copper level of 3.91 µg/L and a freshwater CCC criterion of 5.58 µg/L (Table 2).

Similarly, copper exceedances were not observed during the July KRBWQM sampling event. Copper levels ranged from undetected to 3.04 µg/L at No Name Creek (duplicate); Beaver Creek resulted in the second highest copper level, 1.77 µg/L (Table 2). Freshwater CCC criteria varied from 4.52 µg/L at three locations in the Kenai River mainstem to 9.62 µg/L at Soldotna Creek (Table 2). While the sample taken at No Name Creek (duplicate) did not result in an exceedance, the copper level reported at this site was 3.04 µg/L and the corresponding freshwater CCC criterion was 6.44 µg/L (Table 2).

Throughout the April sampling event, zinc levels ranged from undetected at three sites to 137 µg/L at Soldotna Creek (Table 3) and freshwater CCC criteria ranged from 39.92 µg/L at No Name Creek to µg/L at Kenai City Docks (Table 3). Exceedances occurred at mainstem sites including Cunningham Park, Kenai River, Pillars, Soldotna Bridge, and Swiftwater Park; tributary exceedances occurred at Beaver Creek, Slikok Creek, and Soldotna Creek.

In contrast, zinc exceedances were not reported during the July KRBWQM sampling event. Zinc levels ranged from undetected at four locations to 69.9 µg/L at Beaver Creek and freshwater CCC criteria ranged from 40.69 µg/L at Swiftwater Park to 86.7 µg/L (Table 3). While the zinc level at Beaver Creek did result in an exceedance, its corresponding freshwater CCC criterion was 79.66 µg/L (Table 3).

Copper and zinc-specific sampling events

During the May sampling event, freshwater CCC criteria for copper ranged from 4.4 µg/L-7.3 µg/L (Table 4). The highest level of copper was noted at No Name Creek (duplicate), 3.27 µg/L, while several sites reported no detection, including Beaver Creek, Slikok Creek, Soldotna Creek, and Jim's Landing (Table 4). When compared to the freshwater CCC criteria, no exceedances were noted during the May sampling event.

Throughout the July sampling event, the freshwater CCC criteria for copper ranged from 4.47 µg/L-9.62 µg/L (Table 4). Calcium and magnesium samples were not taken at the Slikok Creek confluence and therefore a freshwater CCC criteria could not be calculated. The highest level of copper was noted at the Slikok Creek confluence, 8.16 µg/L, while the lowest level was estimated at 0.39 µg/L at No Name Creek (Table 4). When compared to the freshwater CCC criteria, no exceedances were noted. However, an exceedance cannot not be determined at Slikok Creek because a freshwater CCC criterion could not be calculated, calcium and magnesium sampling was not conducted at this site.

Zinc samples taken during the May sampling event resulted in zinc levels that ranges from undetected at all three mainstem sites to 159 µg/L at No Name Creek (duplicate) (Table 5). The second highest zinc level was also recorded from another sample taken at No Name Creek, 98.1µg/L (Table 5). Freshwater CCC criteria ranged from 32.59 µg/L at No Name Creek (both samples) to 86.7 µg/L at Soldotna Creek (Table 5). Freshwater CCC criteria could not be calculated at Slikok Creek confluence because calcium and magnesium samples were not taken at this site during the April KRBWQM sampling event. This spring sampling event resulted in exceedances from samples taken at No Name Creek (both samples), Beaver Creek, and Slikok Creek-all tributaries of the mainstem Kenai River.

The July sampling event resulted in zinc levels that varied from undetected at four locations to 64.4 µg/L at Beaver Creek. Freshwater CCC criteria ranged from 40.56 µg/L at Skilak Lake outlet to 86.7 µg/L at Soldotna Creek (Table 5). This value could not be calculated for Slikok Creek confluence because a calcium and magnesium sample was not taken at this site during the July KRBWQM sampling event. While the July sampling event did not result in any exceedances, the sample analyzed from Beaver Creek resulted in a zinc level of 64.4 µg/L and a freshwater CCC criterion of 79.66 µg/L (Table 5).

Mapping potential sources of copper and zinc

Potential sources on the Kenai River

In total, 932 photos were taken of RR parcels and 899 photos were taken of RL parcels with potential copper and zinc sources. These photos have been imported into ESRI's ArcMap program. An attribute table will be created for all photos and will contain information such as parcel ID, the number of potential metal sources, and the type of potential source observed on the property. To date, potential sources documented included elevated, light-penetrating walkways; building roofs; impervious surfaces such as roads and parking lots; significant erosion; boat launches; bridges; and RV parks. This is an ongoing process and the resulting shapefile will be incorporated with the data included in the mapping described below. Findings will be summarized in the 2020 final draft submitted to ADEC under this grant.

Potential sources throughout the Kenai River watershed

While these mapping efforts are ongoing, potential sources of these metals include road construction, gravel pits, stormwater discharge, stormwater treatment structure/outfall, boat launches, impervious surfaces, densely populated areas, golf courses, wastewater treatment plants, and airports. A shapefile has been created to visually document these sources and will be used to as a powerful mapping to identify areas of high-concentrated potential sources of copper and zinc. Findings will be summarized in the 2020 final draft submitted to ADEC under this grant.

DISCUSSION

Copper and zinc sampling

Kenai River Baseline Water Quality Monitoring (KRBWQM)

Copper exceedances were not observed during the 2019 KRBWQM April and July sampling events. Beaver Creek and No Name Creek (duplicate) samples did result in copper levels that approached their freshwater CCC criteria in April and July, respectively. In addition, copper levels detected at the Kenai City Dock resulted in levels roughly 1 µg/L and 2 µg/L (duplicate) higher than those collected throughout the watershed, though their freshwater CCC criteria were significantly higher than those calculated for the rest of the watershed (70.9 µg/L and 35.43 µg/L, respectively) (Table 2). Kenai City Dock (duplicate) and Beaver Creek results both showed decreases in copper levels from spring to summer. This could be a result of increased snowmelt and rain events (see "General discussion: zinc exceedances"). Sample analysis for copper will continue at these sites in order to monitor them for any future exceedances or trending changes over time.

While zinc exceedances were not reported during the July sampling event, eight exceedances were identified during the April sampling event. Mainstem exceedances occurred at Cunningham Park, Kenai River, Pillars, Soldotna Bridge, and Swiftwater Park sampling sites; tributary exceedances occurred at Beaver Creek, Slikok Creek, and Soldotna Creek. Notably, the duplicate sample taken at Slikok Creek reported an undetectable level of zinc, warranting further investigation at this site in future years. Exceedances noted in April were taken during a period of snowmelt and at sites located within highly-developed areas of the Kenai Peninsula and are all located throughout the general City of Soldotna and City of Kenai area (see "General discussion: zinc exceedances").

Copper and zinc-specific sampling events

It is critical to note that the freshwater CCC criteria for both May and July sampling events were calculated using calcium and magnesium levels obtained from April and July KRBWQM sampling events, respectively. Copper and zinc-specific spring sampling was conducted on May 22, 2019 while the calcium and magnesium samples used to calculate hardness were taken during the KRBWQM event on April 30, 2019. Samples collected during the copper and zinc-specific summer event were collected on July 24, 2019 while the calcium and magnesium samples were taken on July 30, 2019. In response, averages of spring and summer calcium and magnesium levels were calculated using data collected from 2000-2014 (Table 6). These averages are intended to be used as reference to which hardness values calculated using KRBWQM calcium and magnesium levels can be compared. Calcium and magnesium samples taken from No Name Creek, Beaver Creek, Slikok Creek, and Soldotna Creek were taken downstream of the copper and zinc-specific samples. A calcium and magnesium sample was not taken at the Slikok Creek confluence during KRBWQM because this is not a site typically included during this biannual sampling program. Moving forward, calcium and magnesium samples will be taken at all sites within the copper and zinc-specific sampling plan and will therefore result in hardness and freshwater CCC criteria that directly correspond to each copper and zinc sample take at each site.

While copper exceedances were not observed during May and July sampling events, there were two notable levels of copper that occurred. In May, the No Name Creek (duplicate) sample resulted in a copper level of 3.27 µg/L and the corresponding freshwater CCC criterion was 4.4 µg/L (Table 4). In July, a copper lever of 8.16 µg/L was recorded at the Slikok Creek confluence site, though a freshwater CCC criterion could not be calculated, as calcium and magnesium samples were not taken at that site (Table 4). Because of the small sample size at the No Name Creek and Slikok Creek confluence sites (n=2 and n=1, respectively), it is highly advised that further sampling is expanded throughout the length of No Name Creek and to a cross-section in the Kenai River at the Slikok Creek confluence.

With the exception of No Name Creek and No Name Creek (duplicate) samples, all copper sampling conducted in July resulted in higher copper levels than in May. However, the freshwater CCC criterion were also higher in July, with the exception of those corresponding to Beaver Creek and Jim's Landing. These increases in copper levels warrant further investigation, though they may be related to the drastic increase in the number of vehicles driven throughout the Kenai River watershed in the summer. Brake pads and tires are commonly-recognized sources on roadways of copper and zinc, respectively. Though the EPA signed a Memorandum of Understanding (MOU) with states and select industry groups to reduce copper in brake pads to 0.5% by 2025, old brake pads with higher copper content will likely remain on roadways for some time. More information regarding this initiative and the associated MOU can be found here: https://www.epa.gov/npdes/copper-free-brake-initiative.

All zinc exceedances were observed during the spring sampling event in May. Slikok Creek, Beaver Creek, and both samples taken at No Name Creek resulted in zinc levels that exceeded their freshwater CCC criteria. Similarly, exceedances occurred during the KRBWQM April sampling event at Beaver Creek and Slikok Creek, when samples were collected near the mouth of these tributaries. These tributaries flow through significant development before reaching the Kenai River, and therefore are adjacent to several potential sources of zinc. More investigation into land development will be conducted and included in the final report of this draft. In addition, they are designated as anadromous streams by the state of Alaska and are known to provide rearing habitat for juvenile salmon (ADFG, 20190). Longitudinal transect of samples collected during the spring would provide further insight into the exact locations of copper and zinc exceedances throughout these anadromous tributaries critical to salmon development.

General discussion: zinc exceedances

It is critical to note that these springtime exceedances in the tributaries and mainstem Kenai River were observed from mainstem RM 0 to RM 23. This stretch of river, primarily located within a section known as the "lower river", flows through the highest concentrations of development that the Kenai River watershed experiences. Located throughout this development are several potential sources of copper and zinc, including thousands of homes, daily tire wear and brake use, motor oil, fertilizer and pesticides (KWF, 2017).

Over winter months, these sources of zinc contribute fine particles that accumulate on surfaces adjacent to these tributaries and mainstem Kenai River. As the season changes, the western Kenai Peninsula experiences increased rainfall and snowmelt events, particularly throughout April when KRBWQM sampling occurs. During a rain or snowmelt event, this build-up may be flushed into adjacent waterbodies, spiking zinc levels. Once suspended in the water column, dissolved metals can be transported further downstream, affecting water quality (Lewis and Clark, n.d.). Metals taken up by aquatic life often prove most toxic when they are in the dissolved phase (Gerhardt, 1993). Because of this toxicity, it remains critical that zinc monitoring continues throughout the Kenai River watershed-an area that Alaska's economy, recreation, and culture rely on and will likely continue to see increased development in coming years.

In order to identify the typical duration of zinc exceedances throughout the Kenai River watershed, it is advisable that zinc is monitored monthly throughout an expanded one-year period under typical rainfall and snowmelt conditions for the area. This would provide further insight into when exceedances occur, which could then be related to the timing of significant events such as rainfall, snowmelt, and glacial melt, in addition to the timing of biological events like salmon smolt outmigration-a period of time when salmon are undergoing several critical physiological changes. Additionally, further literature review is required in order to identify the detrimental effects zinc exceedances can have on the juvenile salmon species that remain in the tributaries for one to two years.

Finally, this study helped identify areas experiencing spring exceedances and will result in a mapping tool that will help identify potential sources of copper and zinc. All efforts are ongoing and will be concluded in 2020 with a final report further detailing area-specific sources of copper and zinc, advisable study expansions, and potential area-specific repercussions of elevated heavy metal levels. Expanding the number of samples taken by way of longitudinal transects within each transect would identify specific areas of metal exceedances, thereby aiding managers in narrowing down potential point sources of copper and zinc in the area. Once specific areas of zinc 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 city planning, wetland preservation, and watershed user and landowner education.

Mapping potential sources of copper and zinc

All mapping of potential sources of copper and zinc throughout the Kenai Watershed is an ongoing effort and will be completed in 2020.

Potential copper and zinc sources: Kenai River

The current shapefile that has been created includes photos taken of parcels with potential sources of copper and zinc along RL and RR. The attribute table corresponding to these photos will be further developed to include attributes such as the number of potential sources, types of potential sources, and parcel ID. This mapping tool could be used to identify areas experiencing significant change overtime, increased development, etc… It is advisable that these photography trips are conducted every 5-10 years in order to update this tool over time.

Potential copper and zinc sources: Kenai River watershed

Identifying potential sources of copper and zinc throughout the Kenai River watershed is an ongoing process. Current methods being employed to identify these potential sources include local knowledge, local contacts, and online searches. Additions to this map could also include critical rearing and/or spawning habitat for salmon, areas of copper and zinc exceedances, and geologic data. Once completed, this shapefile will be integrated with the photo shapefile described above. This will result in a powerful mapping tool that will be used to identify areas such as those that contain highly-concentrated potential copper and zinc sources. In order to maintain relevancy, though, KWF highly recommends that the data contained within this mapping tool is updated on an annual bases in order to track changes in development over time.

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. 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 during the spring and summer, much remains to be known about temporal variation and point sources of these heavy metals. As a result, the following preliminary study expansions are advised:

1. **Complete copper and zinc sampling as well as mapping of potential sources through 2020**
    a. Collect additional calcium and magnesium samples at each copper and zinc-specific sampling site
    b. Identify critical areas of copper and zinc exceedances
    c. Identify critical areas of highly-concentrated potential sources of copper and zinc using mapping tool
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 spring zinc 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
3. **Track changes in development throughout the Kenai River watershed to address anthropogenic impact over time**
    a. Conduct Kenai River photography trips every 10 years
    b. Monitor new development over time in order to conduct annual updates of mapping tool
4. **Develop an educational program for local land owners and watershed user groups including topics such as responsible river use and effective property restoration projects**
    a. Implement restoration and other mitigation efforts through local partnerships to encourage bioretention of heavy metals

It would be a resource-intensive process to attempt to identify all point sources at each sampling site reporting metal exceedances, as these are location-dependent. However, the Kenai River watershed boasts one of the largest water quality datasets in the state of Alaska-an invaluable resources showing a concerning history of heavy metal exceedances throughout the watershed. Expanding this study would aid in a more detailed delineation of spatial and temporal variations of these exceedances in the Kenai River watershed. As adjacent development and subsequent riparian devegetation increase along the Kenai River mainstem and its tributaries, study expansion remains a critical step that would lead to effective, strategic mitigation efforts throughout this highly-revered watershed in Alaska.

REFERENCES

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APPENDIX A: MAPS

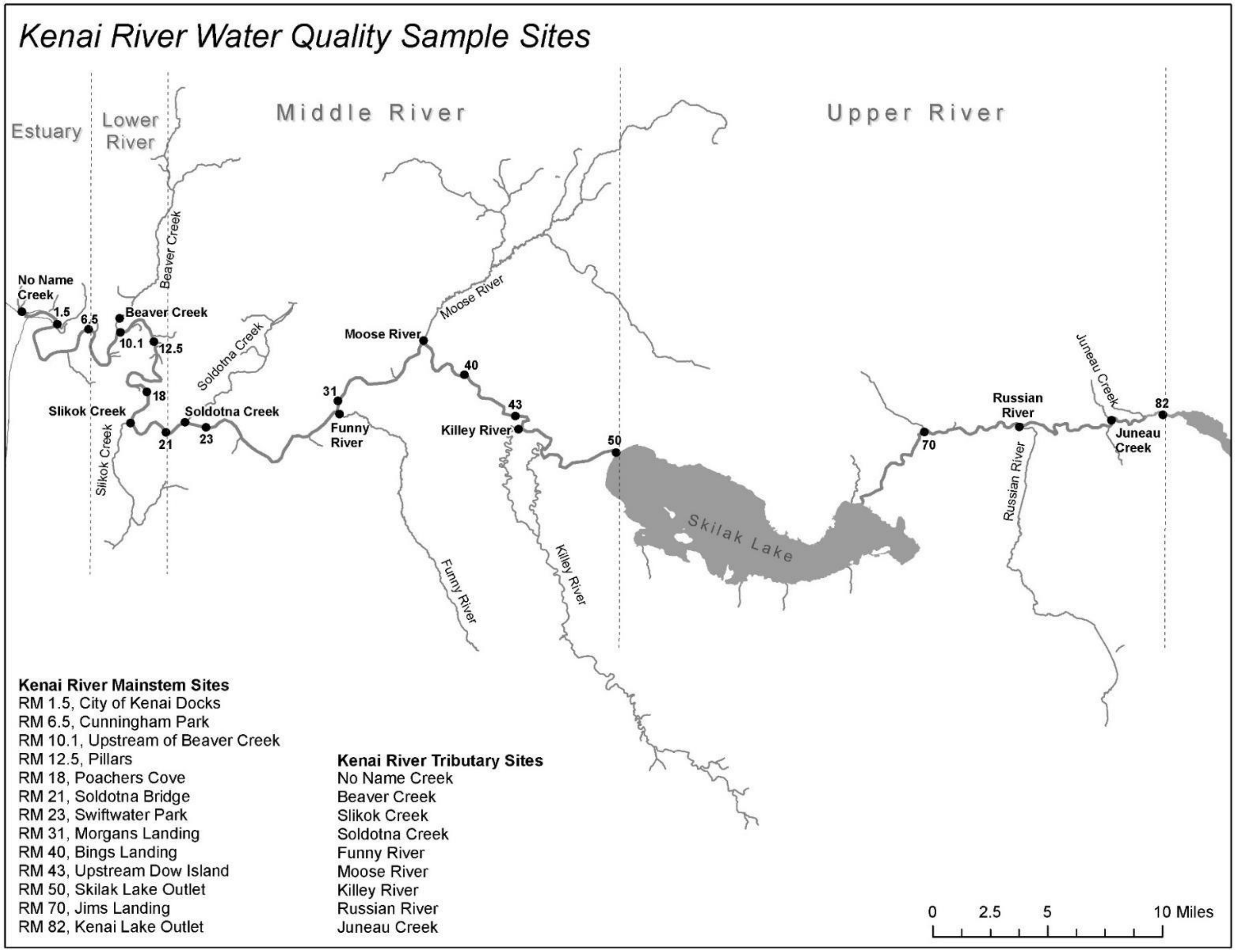

FIGURE 1. DIVISION OF THE KENAI RIVER WATERSHED (LOWER, MIDDLE, AND UPPER KENAI RIVER) AND WATER QUALITY MONITORING SITE LOCATIONS DURING KRBWQM SAMPLING EVENTS.

FIGURE 2. 2019 COPPER AND ZINC-SPECIFIC SAMPLING LOCATIONS ALONG THE KENAI RIVER MAINSTEM AND ITS TRIBUTARIES.

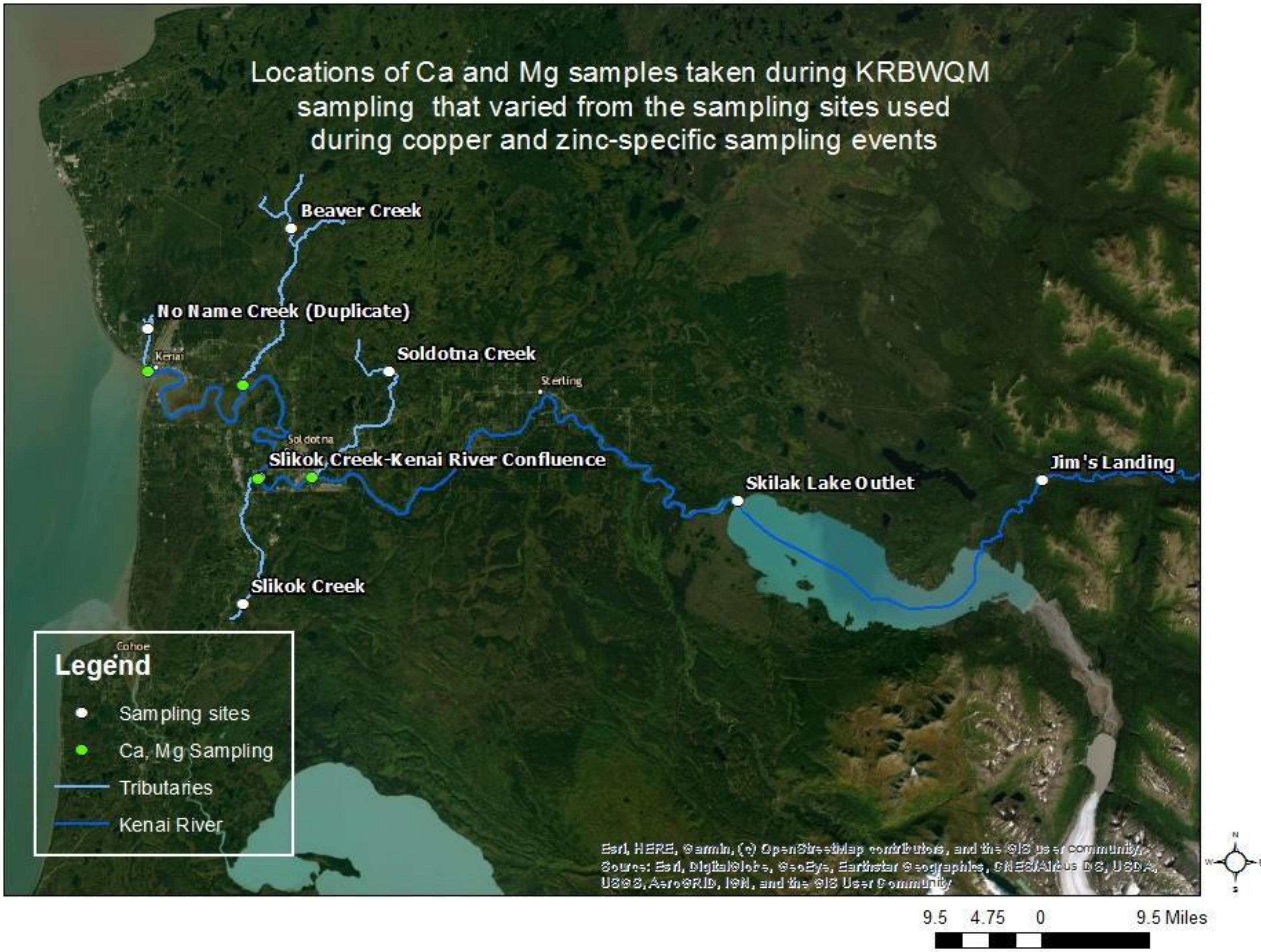

FIGURE 3. SAMPLING LOCATIONS OF CALCIUM AND MAGNESIUM FOR SAMPLES TAKEN DURING KRBWQM IN APRIL AND JULY WHOSE LOCATIONS VARIED FROM THEIR CORRESPONDING COPPER AND ZINC SAMPLING LOCATIONS DURING COPPER AND ZINC-SPECIFIC SAMPLING IN 2019.

APPENDIX B: TABLES

TABLE 1ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION WATER QUALITY STANDARDS AND PERTAINING CALCULATIONS.

Parameter	ADEC Standard	Reference
Copper	$(e^{0.8545(\ln \text{hardness*})-1.702})*0.96$ 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	$(e^{0.8473(\ln \text{hardness*})+0.884})*0.986$ 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*	2.497(Ca mg/L) + 4.119(Mg mg/L)	Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (Eds.), 1998, Standard Methods for theExamination of Water and Wastewater (20th ed.), Washington D.C.: AmericanPublic Health Association, American Water Works Association, and Water Environment Federation.

TABLE 2. COPPER LEVELS AND HARDNESS-DEPENDENT STANDARDS FOR SAMPLING EVENTS ON KENAI RIVER MAINSTEM AND TRIBUTARIES ON APRIL 30, 2019 AND JULY 30, 2019 DURING BIANNUAL KRBWQM SAMPLING EVENTS.

	River mile	Site name	Location on Kenai River	Cu (ug/L)	Hardness (mg/L)	Standard: CCC (ug/L)
4/30/2019	0.0	No Name Creek	Tributary	0.67J	32.59	4.40
	1.5	Kenai City Dock	Mainstem	2.49	842.68	70.90
	1.5	Kenai City Dock-DUP	Mainstem	1.68	374.19	35.43
	6.5	Cunningham Park	Mainstem	0.75J	36.84	4.89
	10.0	Beaver Creek	Tributary	3.91	43.06	5.58
	10.1	Kenai River	Mainstem	0.66J	34.23	4.59
	12.5	Pillars	Mainstem	0.68J	33.90	4.55
	18.0	Poacher's Cove	Mainstem	0.47J	34.53	4.62
	19.0	Slikok Creek	Tributary	0.78J	38.74	5.10
	19.0	Slikok Creek-DUP	Tributary	0.5U	38.45	5.07
	21.0	Soldotna Bridge	Mainstem	0.72J	33.49	4.50
	22.0	Soldotna Creek	Tributary	0.6J	58.94	7.30
	23.0	Swiftwater Park	Mainstem	0.46J	34.11	4.58
	30.0	Funny River	Tributary	0.36J	34.41	4.61
7/30/2019	0.0	No Name Creek	Tributary	0.45J	51.22	6.48
	0.0	No Name Creek-DUP	Tributary	3.04	50.85	6.44
	1.5	Kenai City Dock	Mainstem	0.56J	74.98	8.97
	6.5	Cunningham Park	Mainstem	0.43J	33.74	4.53
	10.0	Beaver Creek	Tributary	1.77	73.65	8.83
	10.1	Kenai River	Mainstem	0.5J	33.62	4.52
	12.5	Pillars	Mainstem	0.45J	33.58	4.52
	18.0	Poacher's Cove	Mainstem	0.42J	33.87	4.55
	19.0	Slikok Creek	Tributary	0.68J	73.58	8.83
	21	Soldotna Bridge	Mainstem	0.49J	33.58	4.52
	22.0	Soldotna Creek	Tributary	0.42U	81.39	9.62
	23.0	Swiftwater Park	Mainstem	0.4J	33.33	4.49
Copper exceedances						
CCC= criterion continuous concentration (freshwater) DUP= duplicate sample J= quantitation is an estimation U= analyte was analyzed for but not detected						

TABLE 3. ZINC LEVELS AND HARDNESS-DEPENDENT STANDARDS FOR SAMPLING EVENTS ON KENAI RIVER MAINSTEM AND TRIBUTARIES ON APRIL 30, 2019 AND JULY 30, 2019 DURING BIANNUAL KRBWQM SAMPLING EVENTS.

	River mile	Site name	Location on Kenai River	Zn (ug/L)	Hardness (mg/L)	Standard: CCC (ug/L)
4/30/2019	0.0	No Name Creek	Tributary	21.30	32.59	39.92
	1.5	Kenai City Dock	Mainstem	89.90	842.68	628.18
	1.5	Kenai City Dock-DUP	Mainstem	110.00	374.19	315.75
	6.5	Cunningham Park	Mainstem	65.60	36.84	44.29
	10.0	Beaver Creek	Tributary	84.10	43.06	50.55
	10.1	Kenai River	Mainstem	67.10	34.23	41.62
	12.5	Pillars	Mainstem	86.00	33.90	41.28
	18.0	Poacher's Cove	Mainstem	5U	34.53	41.92
	19.0	Slikok Creek	Tributary	74.40	38.74	46.22
	19.0	Slikok Creek-DUP	Tributary	5U	38.45	45.92
	21.0	Soldotna Bridge	Mainstem	56.40	33.49	40.85
	22.0	Soldotna Creek	Tributary	137.00	58.94	65.96
	23.0	Swiftwater Park	Mainstem	59.60	34.11	41.49
	30.0	Funny River	Tributary	5U	34.41	41.80
7/30/2019	0.0	No Name Creek	Tributary	5.53J	51.22	58.56
	0.0	No Name Creek-DUP	Tributary	5.31J	50.85	58.20
	1.5	Kenai City Dock	Mainstem	5J	74.98	80.87
	6.5	Cunningham Park	Mainstem	5U	33.74	41.12
	10.0	Beaver Creek	Tributary	69.90	73.65	79.66
	10.1	Kenai River	Mainstem	10.70	33.62	40.99
	12.5	Pillars	Mainstem	8.14J	33.58	40.94
	18.0	Poacher's Cove	Mainstem	5U	33.87	41.25
	19.0	Slikok Creek	Tributary	4.01J	73.58	79.60
	21	Soldotna Bridge	Mainstem	5U	33.58	40.94
	22.0	Soldotna Creek	Tributary	5U	81.39	86.70
	23.0	Swiftwater Park	Mainstem	3.49J	33.33	40.69
Zinc exceedances						

TABLE 4. COPPER LEVELS AND FRESHWATER HARDNESS-DEPENDENT STANDARDS FOR SAMPLING EVENTS ON KENAI RIVER MAINSTEM AND TRIBUTARIES ON MAY 22, 2019 AND JULY 24, 2019 DURING COPPER AND ZINC-SPECIFIC SAMPLING EVENTS. HARDNESS WAS CALCULATED USING LEVELS OF CALCIUM AND MAGNESIUM FOUND DURING THE KRBWQM SAMPLING EVENTS (TABLE 1).

	River mile	Site name	Location on Kenai River	Cu (ug/L)	Hardness (mg/L)	Standard: CCC (ug/L)
5/22/2019	0.00	No Name Creek	Tributary	0.53J	32.59	4.40
	0.00	No Name Creek (DUP)	Tributary	3.27	32.59	4.40
	10.00	Beaver Creek	Tributary	0.5U	43.06	5.58
	19.00	Slikok Creek Confluence	Mainstem	0.42J	NA	NA
	19.00	Slikok Creek	Tributary	0.5U	38.45	5.07
	22.50	Soldotna Creek	Tributary	0.5U	58.94	7.30
	50.00	Skilak Lake Outlet	Mainstem	0.37J	32.72	4.42
	70.00	Jim's Landing	Mainstem	0.5U	42.94	5.57
7/24/2019	0.00	No Name Creek	Tributary	0.39J	50.85	6.44
	0.00	No Name Creek (DUP)	Tributary	0.61J	50.85	6.44
	10.00	Beaver Creek	Tributary	1.07	73.65	8.83
	19.00	Slikok Creek Confluence	Mainstem	8.16	NA	NA
	19.00	Slikok Creek	Tributary	0.53J	73.58	8.83
	22.50	Soldotna Creek	Tributary	0.81J	81.39	9.62
	50.00	Skilak Lake Outlet	Mainstem	0.70	33.20J	4.47
	70.00	Jim's Landing	Mainstem	0.64	40.07J	5.25
Copper exceedances						

TABLE 5. ZINC LEVELS AND FRESHWATER HARDNESS-DEPENDENT STANDARDS FOR SAMPLING EVENTS ON KENAI RIVER MAINSTEM AND TRIBUTARIES ON MAY 22, 2019 AND JULY 24, 2019 DURING COPPER AND ZINC-SPECIFIC SAMPLING EVENTS. HARDNESS WAS CALCULATED USING LEVELS OF CALCIUM AND MAGNESIUM FOUND DURING THE KRBWQM SAMPLING EVENTS (TABLE 1).

	River mile	Site name	Location on Kenai River	Zn (ug/L)	Hardness (mg/L)	Standard: CCC (ug/L)
5/22/2019	0.00	No Name Creek	Tributary	98.10	32.59	39.92
	0.00	No Name Creek (DUP)	Tributary	159.00	32.59	39.92
	10.00	Beaver Creek	Tributary	77.80	43.06	50.55
	19.00	Slikok Creek Confluence	Mainstem	5U	NA	NA
	19.00	Slikok Creek	Tributary	67.60	38.74	46.22
	22.50	Soldotna Creek	Tributary	48.50	58.94	65.96
	50.00	Skilak Lake Outlet	Mainstem	5U	32.72	40.06
	70.00	Jim's Landing	Mainstem	5U	42.94	50.43
7/24/2019	0.00	No Name Creek	Tributary	5.12J	50.85	58.20
	0.00	No Name Creek (DUP)	Tributary	5.77J	50.85	58.20
	10.00	Beaver Creek	Tributary	64.40	73.65	79.66
	19.00	Slikok Creek Confluence	Mainstem	3.55J	NA	NA
	19.00	Slikok Creek	Tributary	5U	73.58	79.60
	22.50	Soldotna Creek	Tributary	5U	81.39	86.70
	50.00	Skilak Lake Outlet	Mainstem	5U	33.20	40.56
	70.00	Jim's Landing	Mainstem	5U	40.07	47.56
Zinc exceedances						

TABLE 6. HARDNESS AVERAGES FOR SAMPLING EVENTS ON KENAI RIVER MAINSTEM AND TRIBUTARIES DURING SPRING AND SUMMER BIANNUAL KRBWQM SAMPLING EVENTS FROM 2000-2014.

	River mile	Site name	Average hardness
Spring	0	No Name Creek	33.22
	10	Beaver Creek	42.96
	19	Slikok Creek Confluence	NA
	19	Slikok Creek	31.47
	22.5	Soldotna Creek	44.21
	50	Skilak Lake Outlet	28.56
	70	Jim's Landing	40.12
Summer	0	No Name Creek	52.60
	10	Beaver Creek	62.75
	19	Slikok Creek Confluence	NA
	19	Slikok Creek	50.84
	22.5	Soldotna Creek	68.73
	50	Skilak Lake Outlet	30.42
	70	Jim's Landing	36.79