

WATER QUALITY EVALUATION OF STREAMS IN THE LIME HILLS ECOREGION OF BRISTOL BAY



Prepared for: Alaska Department of Environmental Conservation

FINAL REPORT submitted on January 30, 2020

Prepared by:

Dr. Birgit Hagedorn

Sustainable Earth Research, LLC

and

Rebecca Shaftel, Dan Bogan, and Leslie Jones

Alaska Center for Conservation Science, UAA

and

Carol Ann Woody

National Park Service

Contents

1. Summary	1
2. Introduction	2
2.1 Background	2
2.2 Project objectives	2
3. Methods	3
3.1 Site selection	3
3.2 Field sampling	3
3.3 Laboratory analysis	5
3.4 Data analysis	6
4. Results and discussion	9
4.1 In-situ water quality parameters	9
4.2 Stream water chemistry	9
4.3 Exceedances of chronic and acute threshold levels	14
4.3.1 Potential effect of sediment geochemistry on exceedances	17
4.4 Water quality at strategic sites	18
4.4.1 Seasonal variations in strategic sites water chemistry	19
4.4.2 Exceedances of chronic and acute threshold levels at strategic sites	22
4.4.3 Evidence of the effect of mineralization on trace metal chemistry in stream water	22
5. Conclusions and future recommendations	25
References	27
Appendices	28

Tables

Table 1. Laboratory analysis procedures with parameters and preservation techniques.	6
Table 2. Field water quality parameters of all sites.	9
Table 3. Maximum, median, and minimum values for hardness calculated with equation (1) and (2) and corresponding acute and chronic values for total and dissolved load derived from the ADEC Toxics Book, [ADEC, 2003].	15
Table 4. Number of sediment samples analyzed in each watershed and percentage of analyses that were above the Low Effect Levels (LEL). (Note: some watersheds that show 100% of samples with exceedances have only one analyzed sample.)	18
Table 5. Exceedances of chronic threshold levels at strategic sites, including samples from TNC.	22

Figures

Figure 1. Map with random and strategic sampling locations and associated watersheds. Study area is outlined in black, yellow watersheds and points indicate strategic sites, and blue watersheds and points indicate random sites. Alaska Department of Natural Resources active state mining claims are shown in brown.	4
Figure 2. Comparing Hardness (1) ($\text{Ca}^{2+} + \text{Mg}^{2+}$) as CaCO_3 and Hardness (2) DIC as CaCO_3	7
Figure 3. The first two factors (PC1 and PC2) of principle components analysis of dissolved load for all streams ($n = 40$) indicating covariation among water quality variables. Points indicate sites and points closer together in the figure have more similar water chemistry regimes than points further apart. Arrows indicate the correlation between water quality parameters and the first two principal components. The direction of the arrow indicates the axis to which that variable is most strongly correlated and the length of the arrow indicates the magnitude of the correlation.	11
Figure 4. Comparison between dissolved and total load for aluminum, arsenic, barium, nickel, iron, and manganese.	12
Figure 5. Comparison of zinc in total load with dissolved organic carbon.	13
Figure 6. Zn total load versus Na (top) and Ca (bottom) concentrations indicating positive and negative correlation for high zinc values.	14
Figure 7. Concentrations of total copper (left) and total zinc (right) are shown with triangles. Acute (red) and chronic (turquoise) threshold levels are shown with points. For zinc, differences in acute and chronic thresholds are minimal and both are shown with turquoise points. Yellow points represent site-specific hardness values, which were used to calculate threshold levels Sites are ordered by decreasing threshold level. Limit of detection (LOD) is the lowest concentration where a substance can be identified with 99% certainty as being present.	17
Figure 8. Location of strategic site watersheds. The Pebble Deposit is located in the headwaters of Upper Talarik Creek and the South and North Forks of the Koktuli River. Watersheds draining to sites ILUTC37 and WIGGLY outlet are directly on top of the deposit.	19
Figure 9. Calcium and aluminum concentrations by Julian day. The dashed lines refer to Julian day 155 = June 4 th and 175 June 24 th when streams were sampled for this report. Colors refer to different watersheds, circles represent data from TNC, and triangles refer to data from this report. Julian day 121 is May 1 st and Julian day 160 is June 9 th	20
Figure 10. Copper in dissolved (upper) and total (lower) load versus Julian Day, The dashed lines refer to Julian day 155 = June 4 th and 175 June 24 th) when streams were sampled for this report. Colors refer to different watersheds, circles represent data from TNC and triangles refer to data from this report. Julian day 121 is May 1 st and Julian day 160 is June 9 th	21

Appendices

Appendix 1. Geologic map of study area with sampling sites from 2015.	28
Appendix 2. Cumulative distribution functions for 31 water quality parameters for small, large, and all streams included in the probabilistic survey design. (Provided in a separate document.).....	29
Appendix 3. In situ water quality and chemical analyses results on the ACCS Data Catalog entry for Bristol Bay Monitoring Data (https://accscatalog.uaa.alaska.edu/dataset/bristol-bay-monitoring-data)......	29
Appendix 4. Summary statistics for water quality parameters analyzed in 40 sampling sites in 2015. Means are shown for four different populations with standard deviations in parentheses. All streams include all 30 randomly-selected sampling sites. Small streams include 12 randomly-selected first and second order streams. Large streams include 18 randomly-selected third and fourth order streams. Strategic streams include ten strategically-selected streams in the southwest portion of the study area. For 25 parameters, more than 50% of the results were below method detection limits and were not included in this table. Results below method detection limits for the remaining parameters were replaced with half the method detection limit for this table.	29
Appendix 5. Correlation between dissolved load and water quality parameters for 2015 sampling data. .	31
Appendix 6. Correlation between total load and water quality parameters for 2015 sampling data.	32
Appendix 7. Correlation between dissolved load and water quality parameters for all strategic sites, including TNC samples.	33
Appendix 8. Correlation between total load and water quality parameters for all strategic sites, including TNC samples.....	34
Appendix 9. Acute and chronic threshold levels for hardness-dependent parameters for dissolved load; based on hardness (1) as CaCO ₃	35
Appendix 10. Acute and chronic threshold levels for hardness-dependent parameters for total load; based on hardness (1) as CaCO ₃	37

1. Summary

This report describes the water chemistry of 40 wadeable streams (1st through 4th order) in the Nushagak and Kvichak watersheds. Mineral exploration over the last decade in a potential hard-rock mining district that straddles the Nushagak and Kvichak watersheds and changes in climate have driven interest in monitoring the stream habitats that make this region so productive for salmon. Samples were collected in June 2015 and analyzed for dissolved and total metals, dissolved organic and inorganic carbon and total nitrogen. In-situ stream chemistry measurements included pH, specific conductance, temperature, and dissolved oxygen. In general, all streams had circumneutral pH and low metal concentrations. Dissolved oxygen (DO) was generally saturated with the exception of four sites in the southern part of the study area (DO < 95%).

The stream chemistry was analyzed in filtered water as dissolved load and in unfiltered water as total load. Metal concentrations for both analyses were compared to acute and chronic threshold levels for aquatic life. Levels were derived from the Alaska Department of Environmental Conservation (ADEC) Alaska Water Quality Criteria Manual for Toxics and Other Deleterious Organic and Inorganics Substances [ADEC Toxics Book, ADEC, 2003] and the National Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQuiRTs) [Buchman, 1999; 2008]. The ADEC Toxics Book provided hardness-based standards for six parameters, which were calculated separately for each site. Hardness is calculated as CaCO₃ from calcium and magnesium concentrations and can potentially lower metal toxicity. Streams with low hardness levels (~ 5 to 60 mg L⁻¹) had low chronic and acute threshold levels making these streams highly vulnerable towards metal toxicity.

Barium and zinc had the highest number of exceedances above chronic threshold levels for aquatic life. Barium exceedances resulted from the very low chronic threshold level of 3.9 µg L⁻¹ published in SQuiRTs. Copper exceedances occurred in the total load for four sites distributed across the study area. Metal concentration exceedances found in stream and lake sediments based on data provided by USGS did not coincide with exceedances found in the stream water suggesting that, when undisturbed, sediment and soil enriched in heavy metals may not affect stream water quality.

A comparison between the dissolved and total load allowed for hypotheses about the form (species) of the elements and their sources. Zinc values in the total load were above 1,000 µg L⁻¹ in 13 streams while zinc in the dissolved load had concentrations below 5 µg L⁻¹. The high zinc concentrations correlated with aluminum in the total load, indicating desorption from inorganic particulate matter that is typically present in higher concentrations during snowmelt runoff.

Eight strategically-selected sites located in the southwest portion of the study area were compared to samples collected by The Nature Conservancy [Zamzow, 2011] in the same streams during three sample events in 2009 and 2010. Both sets of results support the assumption that snowmelt transports metals bound on mineral surfaces to the stream water. Elevated concentrations of copper in total and dissolved load were found during summer baseflow indicating its relation to weathering of sediments and rocks.

The results presented here highlight the need for additional baseline monitoring of stream water chemistry in the study area to answer basic research objectives. The 2015 data collected for this report are a snapshot from the early summer season only and may not reflect the chemistry from other seasons of the year, including spring snowmelt and fall, when higher flows may mobilize particles and metals. We were able to incorporate additional data collected by TNC that overlapped some of our sites, but publicly available data for this region is limited. Data collected by the Pebble Limited Partnership over multiple seasons and years are not available in a digital format that can be analyzed, which makes comparisons with our dataset

difficult.¹ We recommend additional sampling of water chemistry parameters across seasons and years to describe how concentrations change over time, calculating exceedances of acute and chronic threshold levels over multiple sampling events to understand potential effects on aquatic biota, and modeling the chemical form of the metals to characterize bioavailability. Future monitoring should include analysis of anions, which would allow for chemical equilibrium modeling. Expanding the availability of baseline monitoring data for this region is necessary to understand overall stream vulnerability to changes in climate and from anthropogenic impacts.

2. Introduction

2.1 Background

The Bristol Bay region is the largest and most valuable wild salmon fishery in the world [Knapp *et al.*, 2013]. The Nushagak and Kvichak watersheds drain approximately half of the Bristol Bay watershed and produce over a third of the total sockeye return to Bristol Bay [EPA, 2014]. Wadeable streams within these large river networks provide essential spawning and rearing habitat to salmon and other important subsistence and sport fish species, while also sustaining productivity of downstream ecosystems via export of nutrients, organic material, and macroinvertebrates. Geology of this area consists mainly of volcanic and plutonic (mostly granitic) rocks and quaternary deposits [Wilson *F.H. et al.*, 2015] as shown in the geological map in Appendix 1. The southern part of the study area includes the granitic rocks of central and southern Alaska along with volcanic rocks of the Meshick unit. In the northern part of the study area, metamorphic sedimentary rocks occur in addition to volcanic and plutonic rocks.

Mineral exploration over the last three decades in a hard-rock mining district that straddles the Nushagak and Kvichak watersheds has driven interest in monitoring stream habitats that support salmon productivity in the region. In 2015, the Alaska Center for Conservation Science (ACCS) at the University of Alaska Anchorage (UAA) sampled 40 wadable streams in the Lime Hills ecoregion of the Nushagak and Kvichak watersheds to develop a baseline of physical habitat, stream biological communities, and water chemistry. This document details methods and results of water chemistry sampling and provides recommendations for future investigations and monitoring.

2.2 Project objectives

The objective of this sampling was to establish a baseline of water quality parameters with respect to aquatic life standards. We addressed four questions with the water quality dataset:

1. Are there exceedances of water quality standards?
2. How do water quality parameter concentrations differ across years at strategic sites?
3. What is the distribution of parameter concentrations across small and large wadeable streams in the study area?
4. Do the data indicate locations of potential mineralization in the study area?

¹ Data collected by the Pebble Limited Partnership (PLP) from 2004 to 2008 were digitized from PDF form by Stratus Consulting in 2011, but a disclaimer on the data prevents publication of the data without authorization from PLP.

3. Methods

3.1 Site selection

A generalized random tessellation survey design (GRTS) was used to randomly-select sites that were spatially balanced across the study area. A total of 30 streams were sampled using the GRTS design, providing the first statistically-robust estimate of stream habitat conditions in the region (Figure 1). Randomly-selected sites (hereafter referred to as random sites) are numbered 1-49 in this report. (Forty-nine sites were evaluated for sampling and 30 were sampled.) Ten additional monitoring sites were strategically selected (hereafter referred to as strategic sites). Historic sampling at five strategic sites indicated potential mineralization in the area: ILUTC37, WIGGLY, MUTSK36, MUTSK35, and MUTST63. The five remaining sites were selected because they are long-term monitoring sites which have been sampled for stream benthic biological communities by ACCS since 2008: ILTNR19, MUEKM23, MUSSM15, MUTSK09, and MUTSK02.

3.2 Field sampling

Streams were sampled between June 1st and June 24th 2015. All sampling was performed within the *stream reach*, which was defined as 40 times the average stream wetted width or 150 meters, whichever was greater. In-situ water chemistry was measured at the center point of the stream reach (X-site). A Hydrolab MS5 probe was held in the stream at mid depth and allowed to equilibrate until measurements had stabilized before recording dissolved oxygen (DO mg/L and % saturation), pH, temperature (T °C), and specific conductance ($\mu\text{S}/\text{cm}$, EC_{25}). The Hydrolab was calibrated each morning using a three-point pH calibration and a one-point calibration for specific conductance (1000 $\mu\text{S}/\text{cm}$). The Hydrolab was calibrated at the site for dissolved oxygen using the percent saturation method.

Water samples were collected at the X-site after in-situ measurements were complete. Samples were collected with nitrile gloves to avoid cross-contamination. Stream water was collected from the mid-channel at mid-depth of the stream into a bottle or syringe while facing upstream. All containers were rinsed three times before filling. For dissolved metals, 40 mL of sample were filtered through a clean 0.45 μm syringe filter. The first 3-5 mL were discarded before filtering into the sample container. Dissolved organic carbon was sampled next using the same syringe and filter. The sample was filtered into a 40 mL carbon-free amber glass bottle and closed with a lid while avoiding the introduction of air bubbles. The total metal samples were collected directly into the sample container without filtration. Field duplicates were collected at approximately 10% of all sites (three total).

An alkalinity sample was collected from the stream and carried to the field laboratory for processing. Alkalinity was measured each evening using the inflection point titration method and following instructions for alkalinity in the [USGS National Field Manual for the Collection of Water Quality Data](#) (Chapter 6.6 Alkalinity and Acid-Neutralizing Capacity).

All water samples were kept cool using frozen gel packs in a cooler until the field crew returned to basecamp in the evening. All water samples were stored in the refrigerator each evening and were transported in a cooler with gel packs to the Applied Science and Engineering Technology (ASET) lab at UAA within 8 days of sample collection to maintain holding times for DOC analysis.

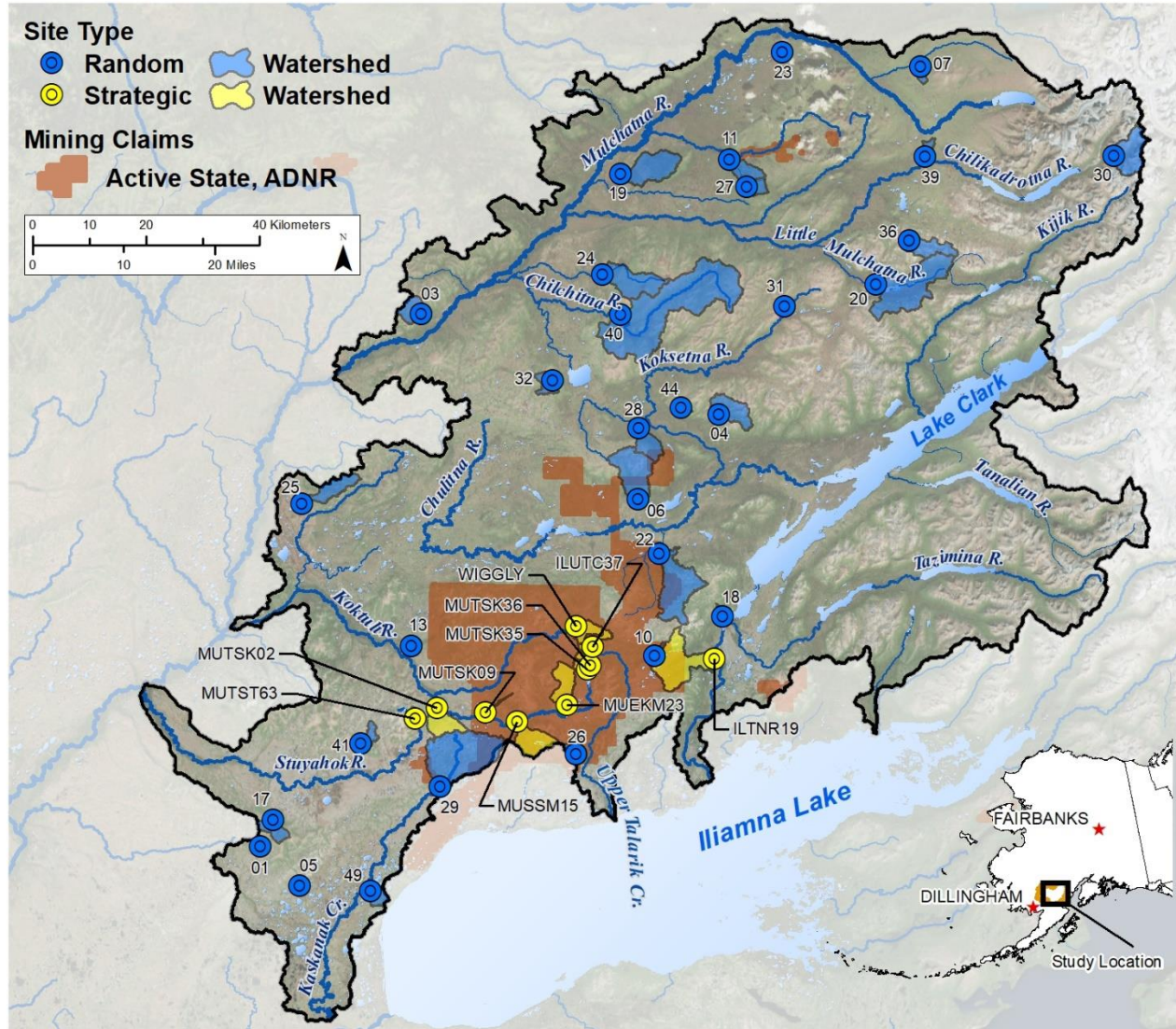


Figure 1. Map with random and strategic sampling locations and associated watersheds. Study area is outlined in black, yellow watersheds and points indicate strategic sites, and blue watersheds and points indicate random sites. Alaska Department of Natural Resources active state mining claims are shown in brown.

3.3 Laboratory analysis

The occurrence and concentration of elements in water samples is controlled by their chemical character and overall physical and chemical conditions of the water body (e.g. temperature, redox conditions, pH, and abundance of complexing organic and inorganic compounds). Elements that maintain ionic form over a wide range of conditions are conservative (unreactive) and remain dissolved in the water. Elements that are reactive may occur as ions, complexes, or attached to surfaces. With some exceptions, elements in ionic form are more bioavailable than those in complexed forms or attached to surfaces. Therefore, it is important to determine the chemical speciation of an element to evaluate its effect on aquatic life. Unreactive elements such as calcium, magnesium, sodium, potassium, and barium are soluble in natural waters resulting in similar concentrations in the total and dissolved loads. Reactive (non-conservative) elements, such as aluminum, cadmium, copper, iron, manganese, lead, and zinc are generally found in higher concentrations in the total load. Iron and manganese tend to form oxo-hydroxides; other elements such as copper form complexes with organic ligands or bicarbonate (HCO_3^-); and cadmium, lead, and zinc attach to organic or inorganic (e.g. iron hydroxides) particle surfaces. Filtration performed in the field for dissolved load samples will eliminate the majority of these compounds from the sample depending on their size. Total load samples are acidified and agitated in the laboratory to release these elements into the water prior to filtration, therefore it is assumed that analyses of total load have higher concentrations of reactive elements compared to analyses of dissolved load. However, it is important to note that the analytical method used here (Inductively Coupled Plasma Mass Spectrometry, ICP MS) will ionize elements bound to small particles (nano) or colloids that have smaller sizes than the nominal pore size of the filter and therefore pass through the filter. Therefore, the distinction between total and dissolved load is defined best by the pore size of the filter, rather than the reactivity of the elements (e.g. ionic versus complexes). For this project, we did not perform the analyses required to determine chemical speciation of elements, but a comparison between the dissolved and total loads, and differences in hardness (alkalinity), pH, and dissolved organic carbon allow us to make some assumptions regarding bioavailability, and metal mobility, which are discussed in the results.

Water samples were analyzed for dissolved metals, total metals, dissolved inorganic carbon, dissolved organic carbon, and total dissolved nitrogen according to standard operating procedures that followed Environmental Protection Agency (EPA) methods. Dissolved metals were analyzed without further sample preparation and using ICP MS (Agilent 7500) with 7 level external calibration (0.1 to $500 \mu\text{g L}^{-1}$) and internal standard mix. The calibration was verified using international NIST standard (SRM 1640a) and continuous calibration standards every 10^{th} sample.

Samples for total metal analysis were further processed in the laboratory. Samples were acidified to pH 2 using concentrated (68-72%) ultrapure nitric acid (HNO_3) and placed for 24 hours on a shaker and then filtered through a $0.45 \mu\text{m}$ syringe filter (GHP Acrodisc 25 mm) into a 15 mL auto-sampler vial. Samples were analyzed with the same instrument and methods as used for dissolved metals but using a different calibration standard due to the potentially higher concentrations in the total metals' samples. A calibration standard with 10x higher concentration in Ca, K, Mg, Na, and Fe compared to other trace metals was used leading to calibration concentrations ranging from $0.5 \mu\text{g L}^{-1}$ to $10,000 \mu\text{g L}^{-1}$.

Dissolved organic carbon (DOC) samples were directly placed on the auto-sampler. A total of $500 \mu\text{L}$ of sample was mixed to 1.5 % v/v with 2N HCl to remove bicarbonate. Ten microliters were injected into a quartz glass furnace and heated to $680 \text{ }^\circ\text{C}$ leading to total combustion of the sample and formation of CO_2 gas and water vapor. Water vapor was removed by vapor scrubber before CO_2 detection by infrared adsorption. Quantitation was performed using external seven level calibration. Blank samples and calibration verification samples were analyzed every 10^{th} sample to monitor analysis performance.

Dissolved inorganic carbon (DIC) was calculated from the difference between total dissolved carbon (TDC) and DOC. TDC was analyzed from the same sample vial as DOC following the same procedure but without acidification of the sample prior to analysis.

Total dissolved nitrogen (TDN) was analyzed together with TDC using nitrogen detector that is in-line with the CO₂ detector.

Table 1. Laboratory analysis procedures with parameters and preservation techniques.

Analysis	Instrument	Parameter	Preservation	Volume
Dissolved Metals	ICP MS, Agilent 7500c	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn	Filtration HNO ₃	45 mL HDPE centrifuge tube
Total Metals	ICP MS, Agilent 7500c	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Si, Th, Tl, U, V, Zn	HNO ₃	45 mL HDPE centrifuge tube
Dissolved Organic Carbon	TOC-VCSH Shimadzu	DOC	Filtration No headspace	40 mL Glass bottle Teflon faced septa
Dissolved Inorganic Carbon	TOC-VCSH Shimadzu	DIC	Filtration No headspace	40 mL Glass bottle Teflon faced septa
Total Dissolved Nitrogen	TOC-VCSH with N detector Shimadzu	TDN	Filtration No headspace	40 mL Glass bottle Teflon faced septa

3.4 Data analysis

Objective 1: Are there exceedances of water quality standards?

Metal concentrations were compared to acute and chronic threshold levels for aquatic life for fresh water listed in the ADEC Toxics Book [ADEC, 2003]. Elemental toxicity depends on the chemical form of a metal in the aquatic environment. Metals are most available and toxic when they occur as metal ion. If compounds are present that can bind to the metal ion, such as bicarbonate (HCO₃⁻), the bioavailability of the metal decreases. If metal analysis only provides the total amount of metals in the water but does not distinguish between metals that occur as pure metal ions or as metal ions bound to other compounds, a correction based on the concentration of such binding compounds has to be made. In this report, ICP MS was used as the analytical instrument, which detects the total amount of metals without distinguishing

between pure metals and metals bound to other compounds. Therefore, a correction for chronic and acute threshold levels was performed for metals that bind to carbonate. The hardness-dependent threshold values were calculated based on hardness expressed as calcium carbonate (CaCO_3) (mg L^{-1}). Two different hardness values were calculated:

- (1) Hardness as CaCO_3 was calculated from the concentrations of calcium ion Ca^{2+} and magnesium ion Mg^{2+} in mg L^{-1} :

$$\text{Hardness} \left(\frac{\text{mg}}{\text{L}} \right) = \left[\frac{\text{Ca} \left(\frac{\text{mg}}{\text{L}} \right)}{\text{MW}_{\text{Ca}}} + \frac{\text{Mg} \left(\frac{\text{mg}}{\text{L}} \right)}{\text{MW}_{\text{Mg}}} \right] \times \text{MW}_{\text{CaCO}_3}$$

- (2) Hardness as CaCO_3 was calculated from the analyzed dissolved inorganic carbon (DIC) concentration in mg L^{-1} :

$$\text{Hardness} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{\text{DIC} \left(\frac{\text{mg}}{\text{L}} \right)}{\text{MW}_{\text{C}}} \times \text{MW}_{\text{CaCO}_3}$$

MW_{Ca} : 40.01

MW_{Mg} : 24.35

$\text{MW}_{\text{CaCO}_3}$: 100.01

MW_{C} : 12.00

The DIC-derived hardness values were higher than the sum of calcium and magnesium values (Figure 2). However, since dissolved inorganic carbon is rarely analyzed with other historic data, we used the hardness (1) value for this report.

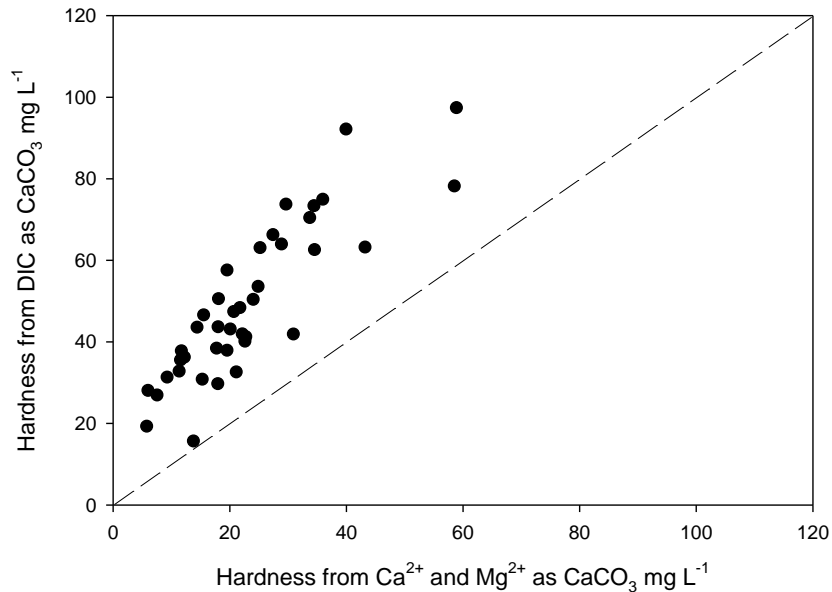


Figure 2. Comparing Hardness (1) ($\text{Ca}^{2+} + \text{Mg}^{2+}$) as CaCO_3 and Hardness (2) DIC as CaCO_3 .

Chronic and acute threshold values for six parameters (cadmium, chromium, copper, lead, nickel, and zinc) were calculated using formulas in the ADEC Toxics Book. Aluminum threshold levels depend on hardness and dissolved organic carbon and were calculated following EPA guidelines for aquatic life in freshwater published in 2018 [EPA, 2018].

All other threshold values for chronic and acute toxicity were derived from the NOAA *Screening Quick Reference Tables* (SQiRTs) [Buchman, 1999; 2008] and are listed in Appendices 9 and 10.

Objective 2: How different are results across years at strategic sites?

Our ten strategic sites are located in the southwest portion of the study area (Figure 1). Eight of the ten streams had been previously sampled by the Pebble Limited Partnership (PLP, unpublished data not for public use) and The Nature Conservancy (TNC) [Zamzow, 2011] between 2004 and 2010. The historic data was compiled into a database by Stratus Consulting for The Nature Conservancy and was provided to ACCS. We combined our results with results from Zamzow [2011] for eight matching streams to compare water chemistry and to evaluate seasonal and inter-annual variability. Although the data cannot be presented in this report, we reviewed PLP data to assess our findings.

Objective 3: What is the distribution of parameter concentrations across small and large wadable streams in the study area?

We described differences in water chemistry between small and large streams by calculating means and standard deviations for all parameters for three populations: small streams ($n = 12$), large streams ($n = 18$), and all streams sampled as part of the probability survey ($n = 30$). For comparison, we calculated the same statistics for our ten strategically-selected streams sampled near to the Pebble deposit. We also tested for significant differences in water chemistry between small and large streams by comparing their cumulative distribution functions (CDFs), which shows the probability that a water quality parameter will be less than or equal to a given concentration. The CDFs for all water quality parameters and three sample populations (small, large, and all streams) are provided in Appendix 2. Prior to analysis, we adjusted sample weights to account for sites not sampled during implementation of the survey design. Sample weights indicate the proportion of streams represented by each site. All analyses were conducted using the *spsurvey* package in the R statistical computing software [Kincaid and Olsen, 2016; R Core Team, 2017].

Objective 4: Do the data indicate locations of potential mineralization in the study area?

The United State Geological Survey (USGS) hosts a database of chemical analyses for stream and lake sediments, which we used to compare bedrock/sediment geochemistry to stream water chemistry. We intersected the watersheds associated with our 40 sample sites with the sediment samples in the USGS database. Watersheds were created for each sample site using a five-meter digital elevation model (DEM) and TauDEM tools (<http://hydrology.usu.edu/taudem/taudem5/>) in ArcGIS. The database included concentrations for major (e.g. aluminum, calcium, magnesium, potassium, sodium, iron), minor (e.g. manganese, titanium), and trace metals and metalloids (e.g. arsenic, barium, cadmium, cobalt copper, lead, zinc). We compared sediment concentrations to SQiRTs Lower Effect Levels (LEL), which represent screening concentrations for inorganic and organic compounds based on EPA regulations and other studies, see also Buchman [1999] and Buchman [2008] for more details.

Principal components analysis (PCA) on a correlation matrix was used to explore covariation between dissolved metals, DOC, DIC, TDN, pH, specific conductance, temperature, and dissolved oxygen. Data were scaled (subtract mean and divide by standard deviation) prior to conducting the PCA. We used a biplot to visualize the PCA results and show differences in water chemistry between sites and covariation among water quality parameters. Arrows on the biplot point in the direction of maximum correlation between a given water quality parameter and the first two principal components (e.g. x and y axes) and the length of the arrow indicates the magnitude of the correlation. We initially proposed chemical equilibrium modeling to determine metal speciation in our samples, but we lacked anion concentrations, which are a requirement for the analysis.

4. Results and discussion

4.1 In-situ water quality parameters

Results for water quality analysis are listed in Appendix 3 and were submitted to ADEC's *Ambient Water Quality Monitoring System* (AWQMS) database. The data are publicly-available on the [ACCS Data Catalog](#). A total of 43 samples were collected from 40 streams (Figure 1): 30 randomly-selected sites and 10 strategically-selected sites. Duplicate samples were collected at three sites and reproducibility was within 20% for the dissolved and total load. Historic data were available for eight of the strategically-selected sites and are included in the discussion of water chemistry at these sites in this report. Summary statistics for the probabilistic sites are provided in Appendix 4 and compared to summaries for the ten strategic sites.

The total ion concentration analyzed as specific conductance ranged from 15.8 to 142 $\mu\text{S cm}^{-1}$ indicating the generally low concentrations and pristine conditions of the sampled streams. The pH values were between 6.3 and 8.6, indicating neutral to slightly alkaline conditions that are within a common range for freshwater streams. Dissolved oxygen ranged from 8.60 to 13.8 mg L^{-1} and oxygen saturation ranged from 88% to 112%. As expected, DO (mg L^{-1}) and temperature were negatively correlated ($r = -0.89$). The lowest DO saturation values were recorded at two tributaries to Kaskanak Creek (site 005, 87.9% and 049, 92.7%), a tributary to the Stuyahok River (MUTSK63, 94.2%), and a tributary to the Chulitna River (022, 94.6%). Water temperatures above 20 °C were recorded in three streams: the Little Mulchatna River (020, 21.9 °C), a tributary to Victoria Creek, (027, 20.2 °C) and a tributary to the North Fork Koktuli River (WIGGLY, 20.6 °C). There was no correlation between DO saturation and stream temperatures. All four sites were low gradient (< 1% slope) streams dominated by slow habitats (pools and runs), indicating reduced stream flow and limited oxygen exchange with the atmosphere.

Small and large streams generally had similar water quality characteristics, with some exceptions. Large streams tended to have higher alkalinity (mean of 26.2 versus 19.4 mg/L CaCO_3 , respectively) and higher specific conductance (65.64 $\mu\text{S/cm}$ versus 56.33 $\mu\text{S/cm}$) (Appendix 4). Instantaneous temperatures for large streams were also approximately 2 °C warmer than small streams, which likely results from decreases in the proportional influence of groundwater and reduced riparian shade, exposing more of the stream surface to long-wave radiation [Caissie, 2006]. Stream temperatures were highest in the strategic streams, averaging 12.3 °C (Appendix 4). Nine of the ten strategically-selected sites were sampled during the third week of the field program, when temperatures were much warmer, which likely impacted this result.

Table 2. Field water quality parameters of all sites.

	pH	Dissolved Oxygen mg/L	Dissolved Oxygen %	Specific Conductivity $\mu\text{S/cm}$	Water Temperature °C
Maximum	8.54	13.8	112	142	21.1
Median	7.33	11.5	99.5	52.9	9.20
Minimum	6.31	8.60	87.9	15.8	2.80

4.2 Stream water chemistry

A total of 43 stream samples were collected and analyzed for 26 elements as total and dissolved load, in addition to dissolved organic carbon, dissolved inorganic carbon and dissolved total nitrogen.

The first two principal components of the PCA explained 41% of the variance in the water quality dataset (Figure 3). Unreactive (or conservative) elements (e.g. calcium, magnesium, and barium) loaded negatively on the first principle component (PC 1 or x-axis) along with specific conductance, pH, and dissolved inorganic carbon. In these streams, specific conductance is mainly explained by calcium and magnesium, which is why conductivity, calcium, magnesium and DIC loaded together on PC 1. Hardness increases the buffer capacity of waters causing a neutral or higher pH value, which explains the correlation between pH, calcium and magnesium, which are components of hardness. Temperature and dissolved oxygen were inversely related and both loaded strongly onto the second principle component, along with reactive elements (iron, manganese, and to a lesser amount aluminum and zinc) and DOC. Most of the strategic sites in the Kaktuli watershed (MUTSK02, MUTSK09, MUEKM23, and MUSSM15) and one site in the Stuyahok watershed (MUTST63) had positive PC 1 scores as these sites had lower pH and specific conductivities. Low pH of water samples favors solubility of reactive elements, which may explain the positive score of aluminum, iron, manganese and zinc on the PC1 axis.

Major ion concentrations followed the order calcium > magnesium > sodium > potassium, with a few exceptions. A tributary of the South Fork Kaktuli River (MUTSK09) had magnesium concentrations above calcium concentrations. At five sites, sodium concentrations were higher than magnesium concentrations: two tributaries to the Mulchatna River (003 and 023), a tributary to the Koksetna River (004), and Victoria Creek (011 and 027), but there was no correlation to bedrock geology that would support the assumption that these changes in water chemistry are related to lithology. The strongest correlations between major ions were between calcium, magnesium, and dissolved inorganic carbon (DIC) in dissolved and total load, indicating that carbonates influence the water chemistry. For trace elements, observed correlations include iron and manganese in the dissolved load and vanadium and aluminum, vanadium and zinc, and zinc and aluminum in the total load. Correlation matrices are provided in Appendices 5 and 6.

Several parameters were significantly different (p -value < 0.05) across the small and large streams included in our probabilistic sample survey. Parameters that increased in concentration downstream included dissolved and total potassium, arsenic, and dissolved manganese. Parameters that had higher concentrations in small headwater systems included dissolved sodium, dissolved nickel, and DOC. Higher DOC in small streams may originate from increased shrub and tree riparian cover relative to stream size. Dissolved organic carbon may decrease pH and bind to trace metals, changing their bioavailability and toxicity. Lower alkalinity and higher DOC in small streams may make them more vulnerable to potential mineral development in the study area, although colder temperatures may increase their resiliency to warming from climate change

We compared the dissolved and total loads for several elements (Figure 4). As expected, the conservative element barium had very similar concentrations between total and dissolved loads. Non-conservative elements, such as aluminum and nickel, had higher concentrations in the total load compared to dissolved load. In contrast, iron and manganese had higher concentrations in the dissolved load than the total load. This is unusual and may indicate that oxi-hydroxides formed between sample collection and acidification of samples in the laboratory (about 2 weeks), which were not dissolved during acidification of samples. The slightly higher concentrations of arsenic in the dissolved load supports this assumption since arsenic co-precipitates easily with iron oxi-hydroxides. The procedure for total load used in this report was acidification and agitation (sonication), which is a soft treatment. The EPA method (EPA 300.5) requires acidification with concentrated nitric acid and heating of samples to 95°C until the sample volume is reduced, which is a much stronger extraction and more likely to dissolve oxi-hydroxides. Other elements, such as cobalt, chromium, copper, and lead, were only detected in the total load, which underscores their reactivity towards particle surfaces (Figure 4).

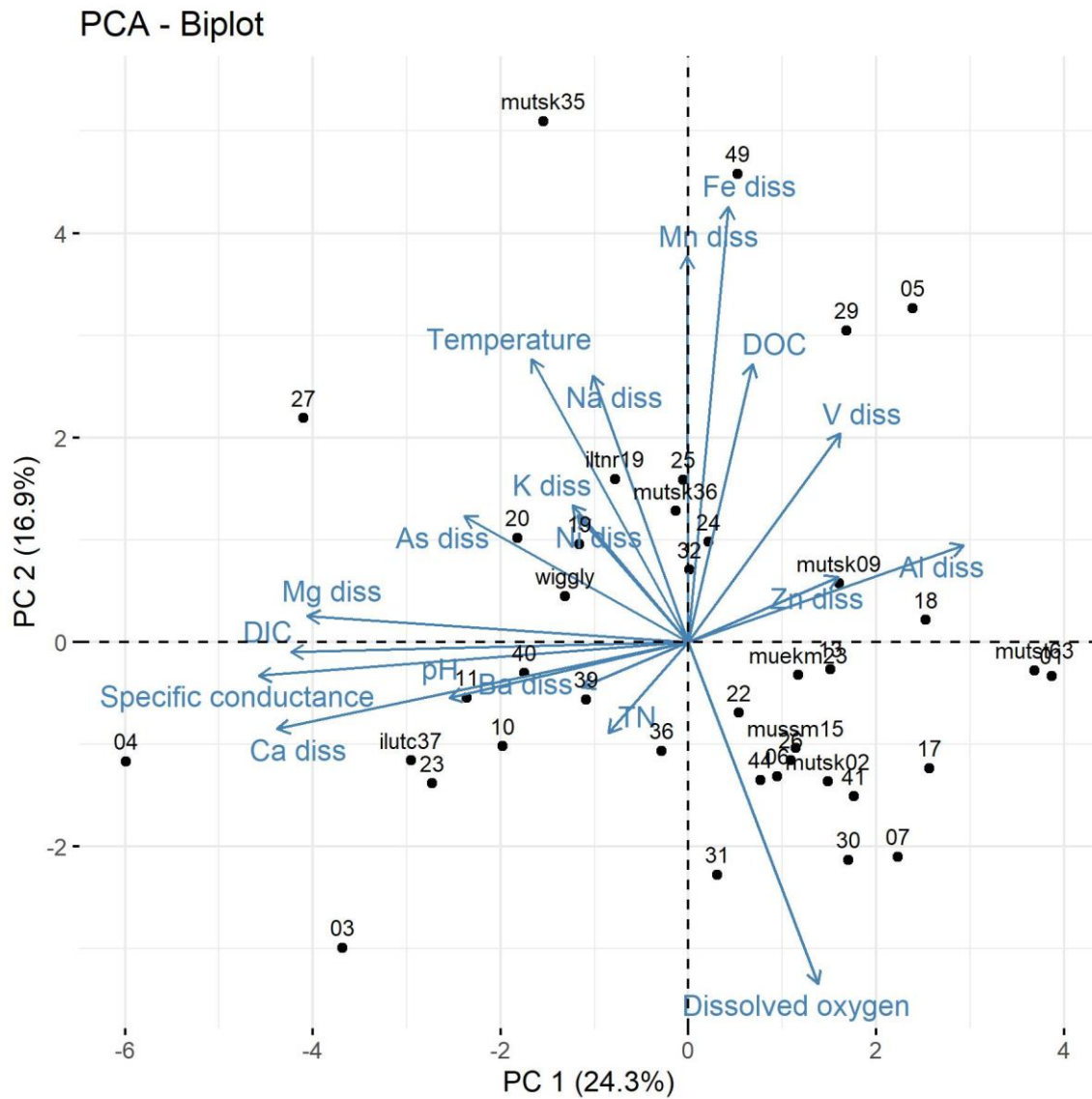


Figure 3. The first two factors (PC1 and PC2) of principle components analysis of dissolved load for all streams ($n = 40$) indicating covariation among water quality variables. Points indicate sites and points closer together in the figure have more similar water chemistry regimes than points further apart. Arrows indicate the correlation between water quality parameters and the first two principal components. The direction of the arrow indicates the axis to which that variable is most strongly correlated and the length of the arrow indicates the magnitude of the correlation.

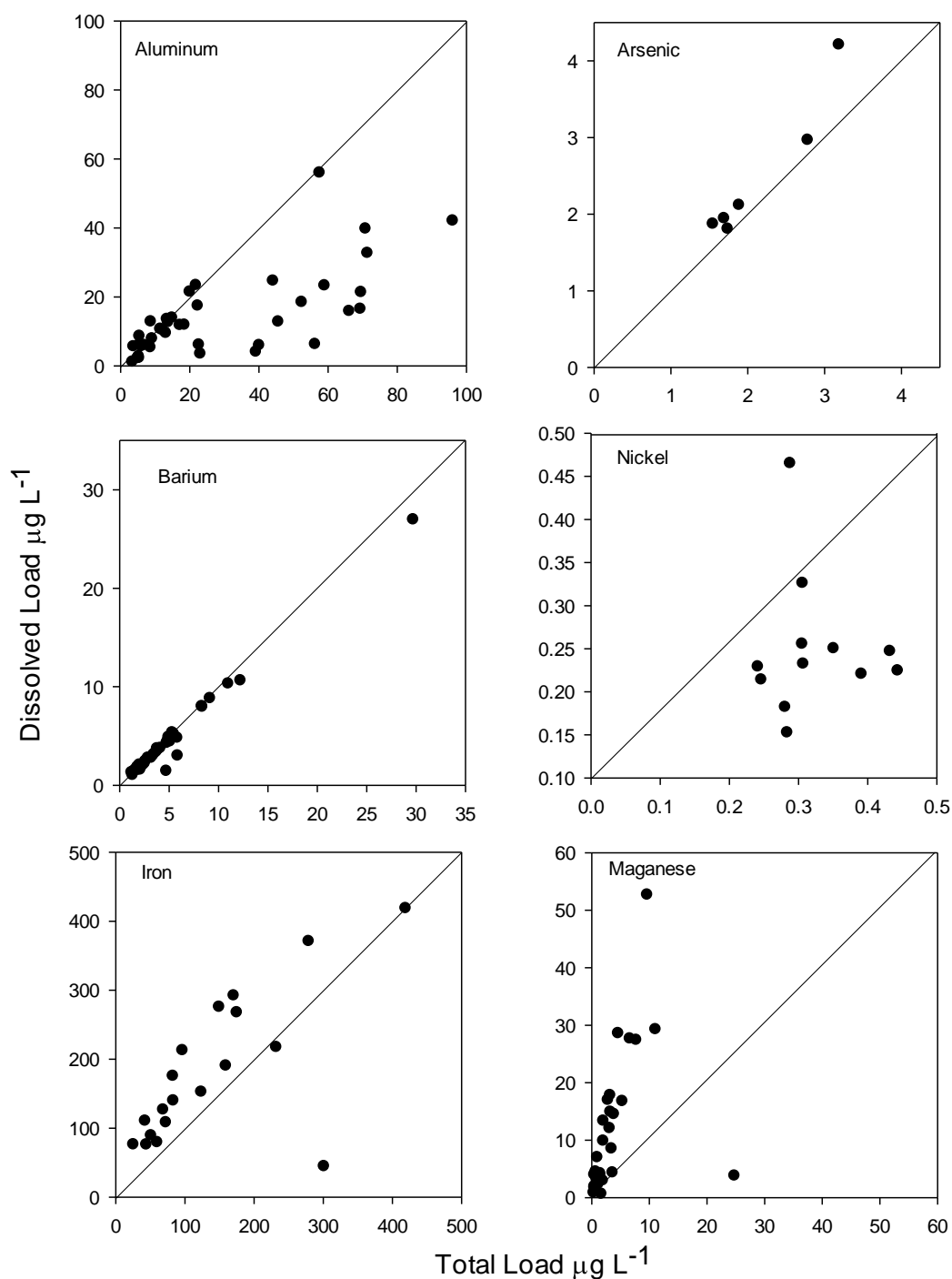


Figure 4. Comparison between dissolved and total load for aluminum, arsenic, barium, nickel, iron, and manganese.

Zinc levels in the total load ranged between 1.43 and 5,850 $\mu\text{g L}^{-1}$ while only three samples of zinc in the dissolved load were above the limit of detection ($3.6 \mu\text{g L}^{-1}$). Zinc occurs in minerals, such as sphalerite (ZnS), or replaces magnesium in silicate minerals, and can be released to water as zinc ion (Zn^{2+}) through weathering. Its speciation in water depends on pH, alkalinity, redox potential, and overall ion concentration in the water. At low pH (< 6), it will mostly occur as zinc ion and at higher pH (> 8), it has a strong tendency

to attach to inorganic surfaces or organic particulate material. If zinc is attached to surfaces or to organic matter, the lowering of pH in an oxic environment leads to release of zinc ions into the water. The high concentration of zinc in the total load indicates that the majority of zinc in these waters is adsorbed onto materials larger than the nominal filter size for dissolved solutes (0.45 μm). There was no correlation between organic carbon and zinc concentrations in the total load, indicating that zinc may have been adsorbed onto inorganic particles (Figure 5). One site, a tributary to the Kaskanak River, (049), had high DOC and total zinc values.

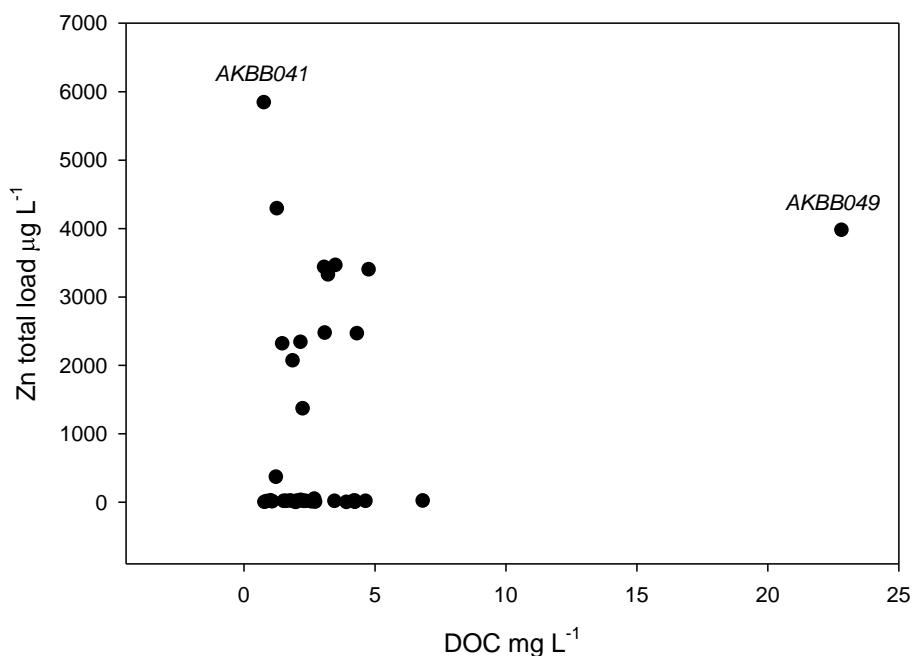


Figure 5. Comparison of zinc in total load with dissolved organic carbon.

The high zinc values were negatively correlated to calcium and positively correlated to sodium (Figure 6), which may indicate that the particulate-bound zinc with high concentrations ($>100 \mu\text{g L}^{-1}$) was responding to specific water chemistry. To gain a better understanding of the high zinc values and their potential threat to the water quality and aquatic life requires additional sampling to confirm the high concentrations over time. Additionally, analysis of anions would allow for chemical speciation modeling, which would reveal more about sources of zinc and its bioavailability [Hogstrand, 2011]. The extremely high zinc concentrations in the total load highlights the potential for zinc toxicity in these streams, especially if physico-chemical characteristics change, such as lower pH or overall ion concentrations in the water, which both can lead to desorption of zinc from surfaces. Zinc was correlated with vanadium and aluminum in the total load ($r = 0.71, 0.80$, respectively) and this suggests that zinc was associated to small particulate matter. Zinc was not correlated with dissolved or total iron providing no evidence of scavenging by iron hydroxides [Stumm and Morgan, 1996]. In addition, vanadium and aluminum were correlated in the total load ($r = 0.67$), but not with iron. This further supports the idea that zinc, aluminum and vanadium are likely associated with mineral matter. Zamzow [2011] found increased aluminum in the total load during snowmelt in streams around the Pebble Prospect compared to samples collected later in the year. This also supports the hypothesis that extremely high zinc values are related to particulate mineral matter trapped and accumulated in snowpack over the winter.

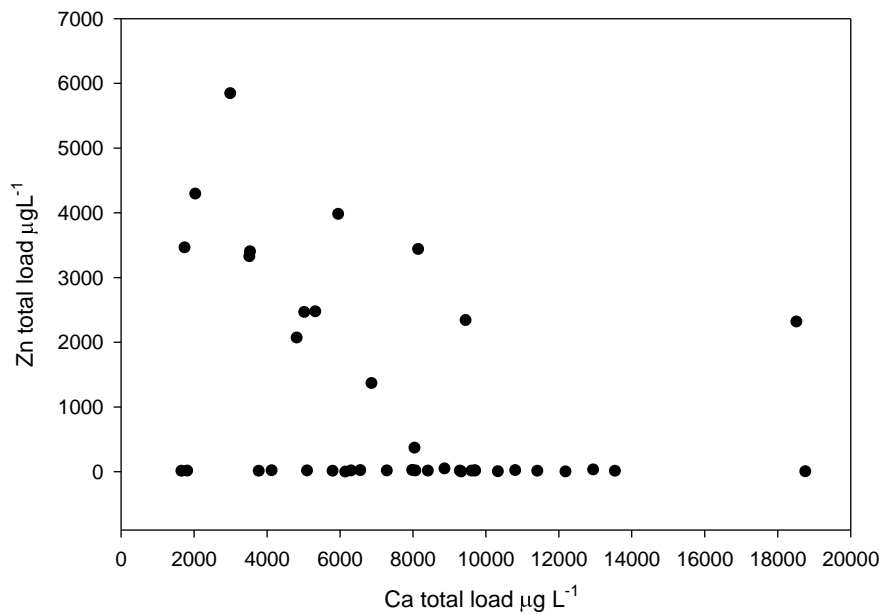
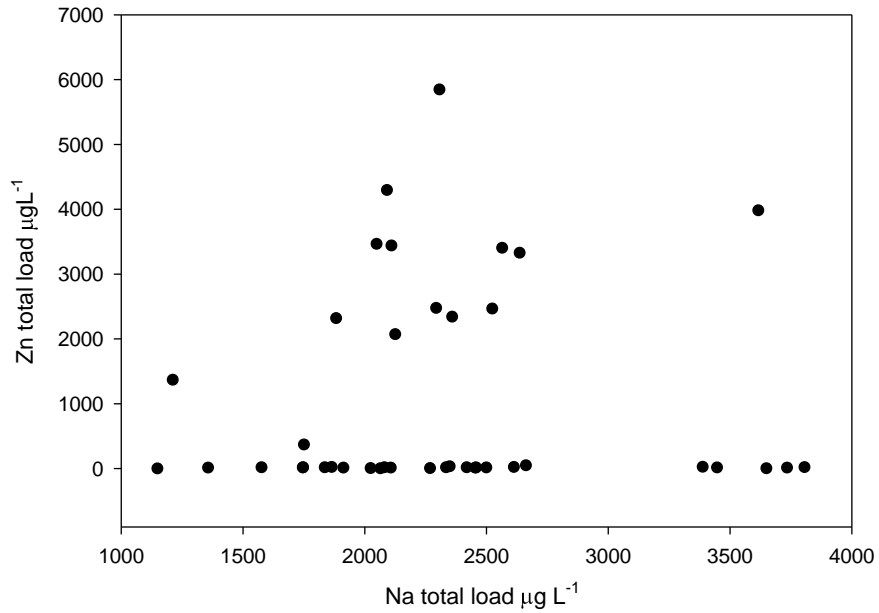


Figure 6. Zn total load versus Na (top) and Ca (bottom) concentrations indicating positive and negative correlation for high zinc values.

4.3 Exceedances of chronic and acute threshold levels

The calculated hardness-dependent acute and chronic threshold levels are listed for all samples in Appendices 9 and 10; Table 3 summarizes these values as maximum, median and minimum values and Figure 7 shows the relationship between acute and chronic threshold values for copper and zinc in the total load and exceedances for each sampling site. Minimum hardness at site 001 was 6 mg L⁻¹ causing chronic

threshold levels for cadmium, copper, and lead to be below $1 \mu\text{g L}^{-1}$. Parameters with the highest number of exceedances of the chronic threshold values were barium in the dissolved (14) and total load (18) and zinc in the total load (17). All exceedances for zinc also exceeded the acute threshold levels (see also Figure 7).

The only other parameter with exceedances in the total load was copper (Site 004). The detection limits for lead and cadmium in the total load were higher than the hardness-dependent chronic threshold limits at four sites. The detection limits for silver, beryllium, cadmium, thallium, and uranium in the dissolved load and for silver, beryllium, and thallium in the total load were above chronic threshold levels for all analyzed samples. There were no aluminum exceedances of the EPA [2018] threshold levels, but two samples exceeded the chronic threshold level in SQuRTs ($87 \mu\text{g L}^{-1}$) for the total load: a tributary to Kaskanak Creek (site 001) and Victoria Creek (028).

Copper exceedances occurred in total load samples collected from a tributary to Summit Creek (site 007, $2.75 \mu\text{g L}^{-1}$), a tributary to Black Creek (028, $23.8 \mu\text{g L}^{-1}$), a tributary to Nikadavna Creek River (032, $3.1 \mu\text{g L}^{-1}$), and a tributary to the South Fork Koktuli River (MUTSK36, $3.53 \mu\text{g L}^{-1}$) (see also Figure 7). There was no correlation between exceedances and threshold levels. The two exceedances above acute threshold for copper were at low and medium hardness.

At four of our sampling sites, the hardness-dependent threshold levels for total cadmium and total lead were below the limit of detection ($0.12 \mu\text{g L}^{-1}$ and $0.20 \mu\text{g L}^{-1}$, respectively). These include a tributary to Kaskanak Creek (001), a tributary of the Stuyahok River (017), and two tributaries to the South Fork Koktuli River (MUTST63 and MUTSK09).

Table 3. Maximum, median, and minimum values for hardness calculated with equation (1) and (2) and corresponding acute and chronic values for total and dissolved load derived from the ADEC Toxics Book, [ADEC, 2003].

	CaCO ₃	Al		Cd		Cu		Pb		Ni		Se	Zn		
	mg L ⁻¹	µg L ⁻¹													
		AC	CR	AC	CR	AC	CR	AC	CR	AC	CR	CR	AC	CR	
Dissolved hardness (1)															
Max	59.0	3400	2100	1.21	0.17	8.18	5.71	36.2	1.41	300	32.7		75.0	75.6	
Median	20.9	1250	545	0.44	0.08	3.08	2.35	11.4	0.28	125	13.7		31.1	31.4	
Min	5.76	360	200	0.12	0.03	0.91	0.78	2.60	0.03	42	4.60		10.4	10.5	
Dissolved hardness (2)															
Max	97.4	3500	2000	1.96	0.24	13.1	8.76	62.8	3.00	458	50.0		115	116	
Median	22.6	1500	580	0.47	0.09	3.31	2.52	12.4	0.32	133	14.6		33.2	33.5	
Min	5.98	450	220	0.13	0.03	0.95	0.81	2.72	0.03	43	4.75		6	4	
Total hardness (1)															
Max	59.0	3400	2100	2.08	1.96	13.7	9.12	79.0	3.08	459	50.6	44.0	117	117	
Median	20.9	1250	545	0.92	0.90	6.41	4.59	28.4	1.11	233	25.6	24.5	59.3	59.3	
Min	5.76	360	200	0.32	0.33	2.44	1.91	7.70	0.30	97.7	10.8	5.00	24.9	24.9	
Total hardness (2)															
Max	97.4	3500	2000	2.08	1.96	13.7	9.12	79.0	3.08	459	50.6	44.0	117	117	
Median	43.6	1500	575	0.92	0.90	6.41	4.59	28.4	1.11	233	25.6	24.5	59.3	59.3	
Min	15.6	450	220	0.32	0.33	2.44	1.91	7.70	0.30	97.7	10.8	5.00	24.9	24.9	

A total of 43% of zinc concentrations in the total load were above chronic and acute threshold levels (Figure 7). There was no correlation between exceedances and threshold levels. The exceedances of zinc were scattered throughout the entire range of acute and chronic threshold values. The geochemistry of these zinc values has been discussed above. It should be highlighted here that such high values need to be verified as they indicate a high risk of zinc toxicity in these streams depending on changes in physico-chemical conditions such as a decrease in pH or an increase in temperature or overall ion concentration. Sites with high zinc values are distributed across the study area but have a higher abundance in the southern part of the study area where mining is proposed.

The dissolved and total load chronic threshold level for barium (3.9 ug L^{-1}) was exceeded at 18 of our sampling sites (45%). Barium occurs in carbonate and sulfate minerals and also replaces calcium in silicate minerals and is naturally released through mineral weathering. Its natural salts (sulfate and carbonate) are highly insoluble, but barium can be introduced to the environment by drilling operations as it is added to drilling fluid [Golding *et al.*, 2018]. Barium toxicity values in SQuiRTs are based on an evaluation described in EcoUpdates, however the referenced web page is no longer available. EPA calculated secondary acute and chronic barium levels to fish and aquatic life as $3,080$ and $171 \text{ } \mu\text{g L}^{-1}$, respectively, for cold water [EPA, 2007]. All of our barium concentrations were below this secondary chronic threshold level. However, Golding *et al.* [2018] highlights that barium's toxicity strongly depends on its solubility and mobility which depends on its speciation. Barium chloride and barium acetate are highly soluble while barium sulfate and barium carbonate are highly insoluble. The large differences in barium solubility make it difficult to evaluate its toxicity to aquatic life without speciation efforts, which require analysis of the anions chloride, sulfate, and carbonate [Golding *et al.*, 2018].

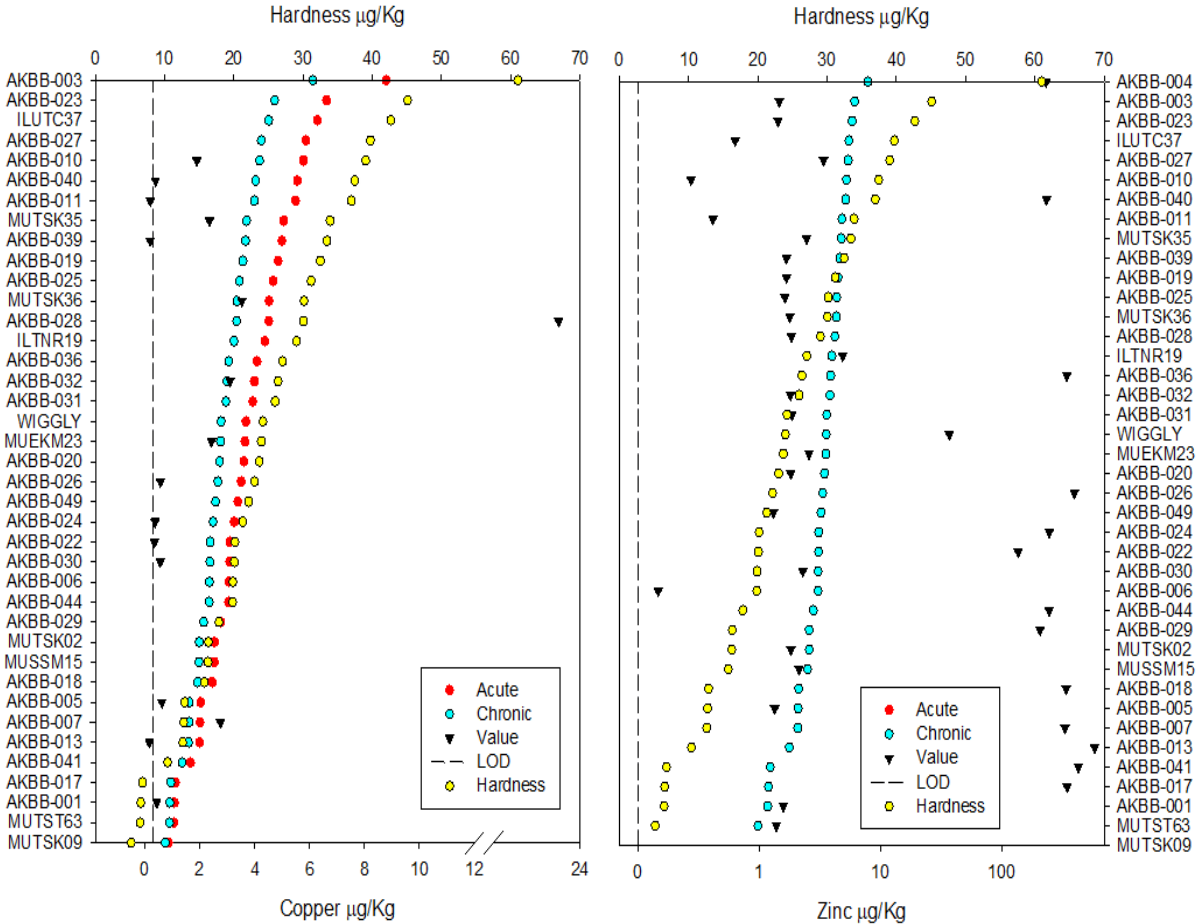


Figure 7. Concentrations of total copper (left) and total zinc (right) are shown with triangles. Acute (red) and chronic (turquoise) threshold levels are shown with points. For zinc, differences in acute and chronic thresholds are minimal and both are shown with turquoise points. Yellow points represent site-specific hardness values, which were used to calculate threshold levels. Sites are ordered by decreasing threshold level. Limit of detection (LOD) is the lowest concentration where a substance can be identified with 99% certainty as being present.

4.3.1 Potential effect of sediment geochemistry on exceedances

A total of 100 USGS sediment samples were collected in 15 of the 40 watersheds for our sample sites (sites 004, 006, 022, 024, 025, 028, 029, 030, 032, 040, 049, ILUTC37, MUEKM23, MUTSK35, MUTSK36, and WIGGLY). A total of 101 analyses resulted in metal concentrations above LELs (Table 4). The elements with the most sediment samples above threshold levels were arsenic, cobalt, chromium, copper, iron, and nickel. Overall, these data highlight the potential risk to aquatic health from geogenic bedrock. High copper values in sediments in the watersheds of sampling sites MUTSK35 and MUTSK36 likely contributed to the stream copper concentrations (the total load for copper in MUTSK36 exceeded the chronic threshold). Zinc sediment values were above LELs in three watersheds (040, 030, and 006). In two of those same watersheds (sites 030 and 006), zinc concentrations were also above acute threshold levels. Besides copper and zinc, the generally low number of exceedances of metals in water samples compared to the high number of sediments that have metal concentrations above LEL suggests that high metal concentrations in sediments do not necessarily contribute to high metal concentrations in stream water in an undisturbed environment. However, disturbances such as production of fresh surfaces through grinding and increase of dust production through transportation of sediment source bedrock has the potential to

increase metal concentrations in aquatic environments through mineral weathering [Anderson and Blum, 2003].

Table 4. Number of sediment samples analyzed in each watershed and percentage of analyses that were above the Low Effect Levels (LEL). (Note: some watersheds that show 100% of samples with exceedances have only one analyzed sample.)

Watershed intercept	Number of samples	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
		0.5	6.0	0.6	50.	26	16	20000	0.2	460	16	31.	120
LEL ($\mu\text{g L}^{-1}$)													
		%											
WIGGLY	3	0	67	0	0	67	0	67	0	0	67	0	0
MUTSK35/36	16	19	100	6	0	94	100	100	0	0	100	0	0
MUEKM23	1	0	100	0	0	100	100	100	0	0	0	0	0
ILUTC37	1	0	100	0	0	100	0	100	0	0	0	0	0
AKBB-049	1	0	100	0	0	0	0	100	0	0	0	0	0
AKBB-040	33	3	67	0	42	97	91	100	0	0	100	15	3
AKBB-032	4	0	100	0	0	100	75	100	0	0	100	0	0
AKBB-030	9	11	33	11	11	89	67	100	0	0	67	33	33
AKBB-029	1	0	0	0	100	100	0	100	0	0	0	0	0
AKBB-028	4	0	100		50	100	50	100	25	0	100	0	0
AKBB-025	4	25	100	0	0	100	0	75	0	0	75	0	0
AKBB-024	4	0	25	0	50	100	75	100	25	0	100	25	0
AKBB-022	5	0	100	0	0	100	60	80	20	0	80	0	0
AKBB-006	6	17	83	0	33	100	83	100	0	0	100	17	17
AKBB-004	9	0	67	0	67	67	56	67	11	0	67	11	0

4.4 Water quality at strategic sites

Correlations between the dissolved and total loads for all samples collected at the ten strategic sites are quite different than what was observed for the samples collected in 2015. No correlations existed between any parameter and zinc for either dissolved or total load. Iron, manganese, aluminum, and vanadium were correlated in the total load indicating their relationship with particulate matter. In the dissolved load, a weak positive correlation between aluminum and dissolved organic carbon and a negative correlation between aluminum and pH was observed. Aluminum solubility increases at lower pH [Stumm and Morgan, 1996]. In addition, a positive correlation existed between copper, iron, manganese and nickel in the dissolved load and between copper, aluminum, iron, manganese and vanadium in the total load.

The absence of a correlation between zinc and aluminum and also the generally much lower values for zinc (5 to 15 $\mu\text{g L}^{-1}$) suggests that the high zinc values may have been related to specific conditions during the 2015 sampling season. The fact that the three duplicate samples collected at sites MUTSK02, 018, and 022 confirm the very high as well as lower zinc concentrations indicate that these values are reproducible. Correlation matrices are displayed in Appendices 7 and 8 for reference.

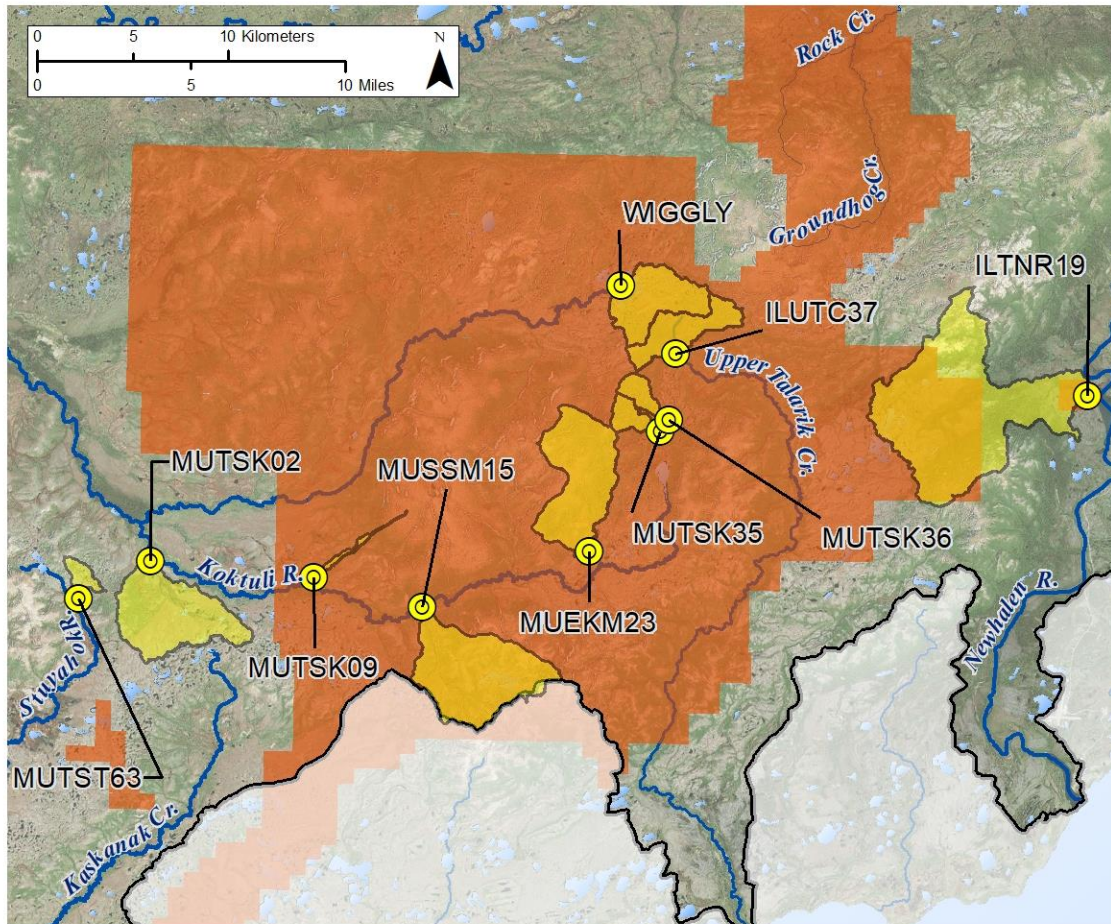


Figure 8. Location of strategic site watersheds. The Pebble Deposit is located in the headwaters of Upper Talarik Creek and the South and North Forks of the Kaktuli River. Watersheds draining to sites ILUTC37 and WIGGLY outlet are directly on top of the deposit.

4.4.1 Seasonal variations in strategic sites water chemistry

Seasonality in this area is mainly driven by winter baseflow, spring snowmelt, summer baseflow, and summer/fall rain events. Snowmelt may be the largest seasonal event and its timing varies based on the elevation of the stream and the watershed it drains. The seasonal sampling of these waters is sparse but some samples from ILTNR19, ILUTC37, MUTSK02, and MUTST63 were sampled in early May (Julian date 121 = May 1st) and early to mid-summer (Julian dates 155 = June 4th to 175, June 24th) and give some insights about changes in chemistry. Calcium in May during snowmelt is lower than during the summer (Figure 9). This indicates the dilution effect of snowmelt on major ion concentrations in streams. In contrast, total aluminum values were higher during spring sampling and decreased in the summer. The higher concentration of aluminum during snowmelt indicates the contribution of aluminum bound to mineral particles (most likely dust) that accumulated in the snow-pack as mentioned by Zamzow [2011]. The positive correlation between aluminum and zinc in the total load observed in all streams sampled for this report supports the idea that high zinc values are attributed to release of zinc from mineral surfaces that were accumulated as dust in snow. In addition to dust entrapped in snow, erosion along river channel and surface erosion may also increase particulate material in stream water.

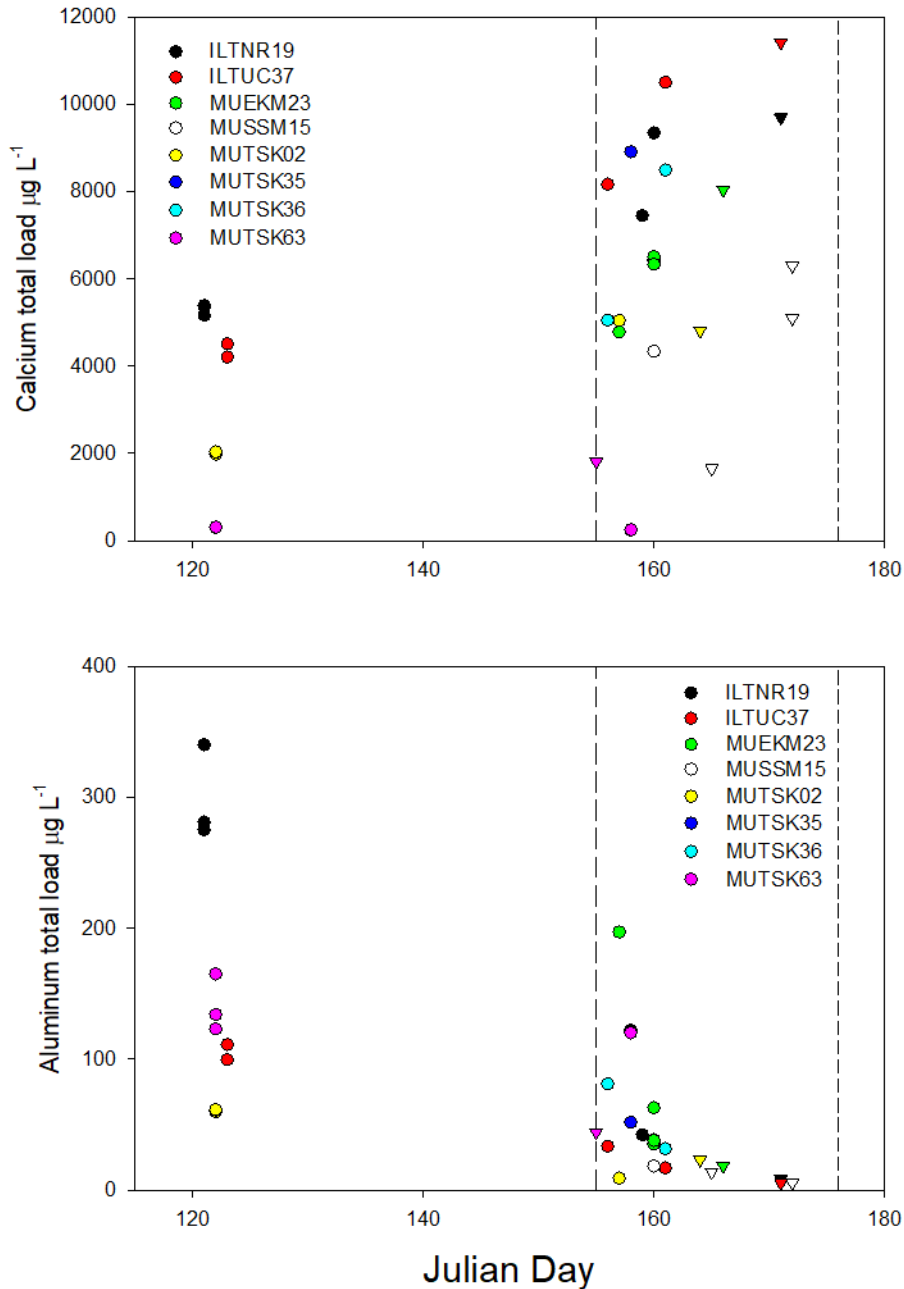


Figure 9. Calcium and aluminum concentrations by Julian day. The dashed lines refer to Julian day 155 = June 4th and 175 June 24th when streams were sampled for this report. Colors refer to different watersheds, circles represent data from TNC, and triangles refer to data from this report. Julian day 121 is May 1st and Julian day 160 is June 9th.

Trace metal concentrations in the dissolved and total load were higher during the beginning of summer than during snowmelt (see copper results in Figure 10) suggesting that weathering of rocks and sediments is the main source and not snowmelt runoff. Highest copper concentrations were observed in watersheds MUTSK36 > MUEKM23 > MUTSK35 (Figure 10), which are closest to the Pebble Prospect area (Figure 8).

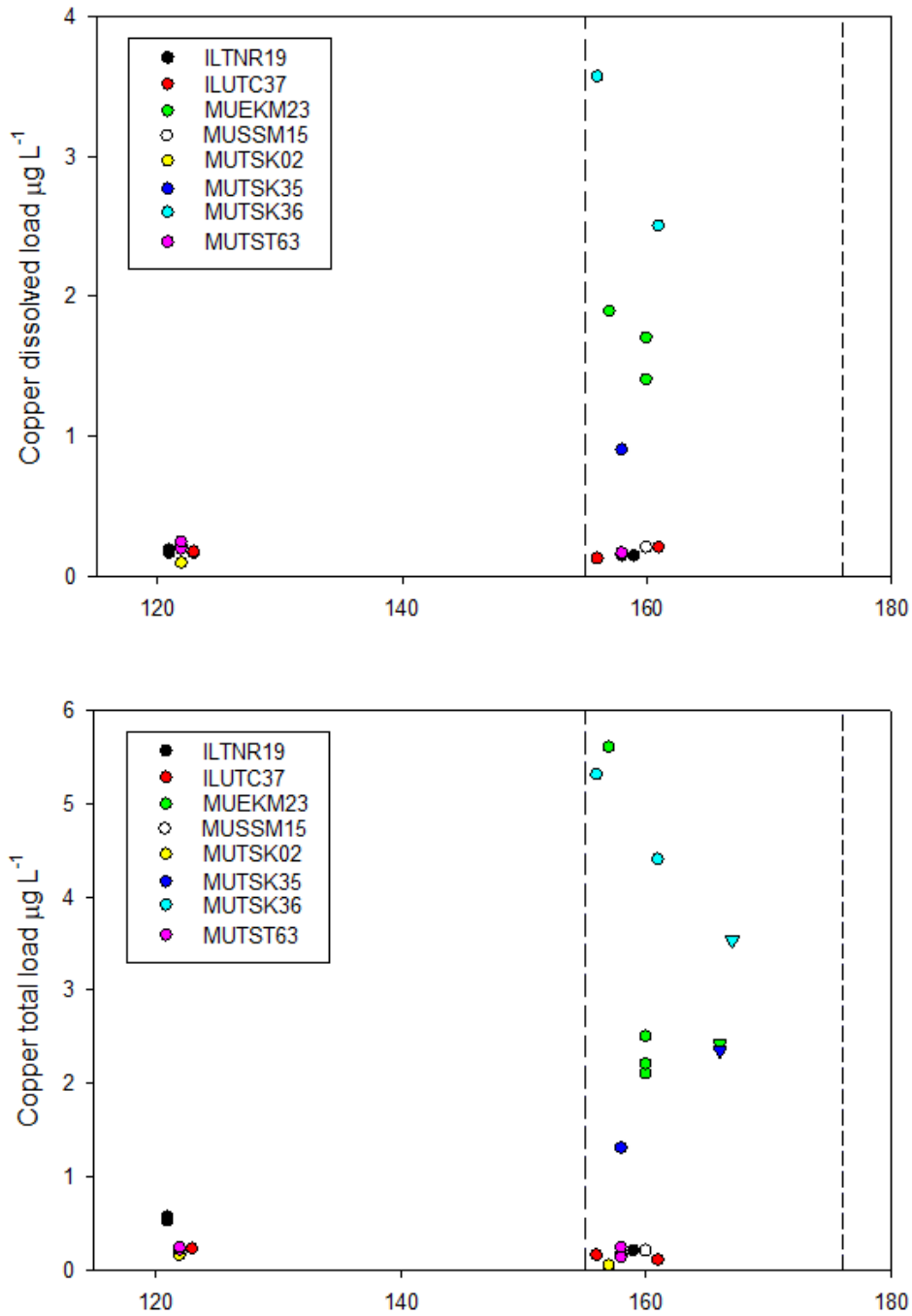


Figure 10. Copper in dissolved (upper) and total (lower) load versus Julian Day. The dashed lines refer to Julian day 155 = June 4th and 175 June 24th) when streams were sampled for this report. Colors refer to different watersheds, circles represent data from TNC and triangles refer to data from this report. Julian day 121 is May 1st and Julian day 160 is June 9th.

4.4.2 Exceedances of chronic and acute threshold levels at strategic sites

We evaluated results from 50 water quality samples collected at the strategic sites over four distinct sampling events. The 50 samples included several field replicates in the TNC dataset, but represent 26 unique sampling events (sites and dates). We summarized water quality exceedances only for unique sampling events. A total of 45 exceedances were calculated for the strategic sites for six different parameters (Table 5). Aluminum chronic threshold levels of $87 \mu\text{g L}^{-1}$ [ADEC, 2003] were used instead of hardness- and DOC-dependent aluminum threshold values because organic carbon data were not available. However, adjusting aluminum exceedances to DOC and hardness will likely increase them above $87 \mu\text{g L}^{-1}$. There were six aluminum exceedances, one in the dissolved load and five in the total load. The exceedance in the dissolved load is from the MUTST63 watershed (tributary to the Stuyahok River) and can be attributed to the low pH (5.4) measured in this stream at the time of sampling. Exceedances (number in brackets) in the total load were from watersheds ILTNR19 (1), ILUT37 (1), MUEKM23 (1), and MUTST63 (2). All exceedances recorded for barium were from samples collected for this report and have been discussed above. Copper exceedances of the chronic threshold level occurred at watersheds MUEKM23 (3), MUTSK36 (4), and MUTST63 (2), with five of the nine samples also exceeding the acute threshold level. Due to the very low calcium and magnesium concentrations in the samples, hardness values were low and acute limits for copper were between 0.180 and $2.72 \mu\text{g L}^{-1}$ and chronic limits were between 0.180 and $5.60 \mu\text{g L}^{-1}$. The chronic level for lead ranged between 0.010 and $0.330 \mu\text{g L}^{-1}$ and samples above the threshold level were from ILTNR19 (1), MUEKM23 (1) and MUTST63 (3), no samples exceeded the acute limits. The chronic levels for zinc ranged from 3.10 to $35.7 \mu\text{g L}^{-1}$ and for acute limits from 3.08 to $35.7 \mu\text{g L}^{-1}$ with samples from MUTSK02 (1), MUTSK09 (1), MUEKM23 (1), and MUTST63 (4) exceeding these thresholds. The majority of exceedances were recorded for the tributary to the Stuyahok River watershed (MUTST63). This site has very low hardness and pH, which results in low threshold levels and a corrosive environment that increases the abundance of ionic form of metals that would otherwise be adsorbed to surfaces.

Table 5. Exceedances of chronic threshold levels at strategic sites, including samples from TNC.

	Total load		Dissolved load	
	counts	relative	counts	relative
Al	5	19%	1	4%
Ba	4	40%	3	30%
Cd	1	4%	0	0%
Cu	6	23%	2	8%
Pb	4	15%	1	4%
Zn	5	19%	1	4%

4.4.3 Evidence of the effect of mineralization on trace metal chemistry in stream water

A total of 21 sediment samples from the USGS data base were located in the watersheds of sampling sites Wiggly, MUTSK36, MUTSK35, MUEKM23 and ILUTC37. Sediment trace metal concentrations for arsenic, cobalt, copper, lead, nickel, and zinc are summarized in box plots in Figure 11. Sediments collected in watersheds MUTSK36 and MUTSK35 showed the highest median concentrations for the majority of elements. The highest zinc concentrations were measured in single samples collected from watersheds MUEKM23 and ILUIT37 (Figure 11).

Boxplots of trace metal concentrations in water samples are shown in Figure 12. Median arsenic concentrations were highest at sites ILTNR19 and MUSK02, whereas median copper concentrations were highest at sites MUEKM23, MUSK35 and MUTSK36. All other trace metal concentrations cover a larger range (25th and 75th percentile box), which overlapped between locations. The small number of water samples collected at each site precludes statistical comparison.

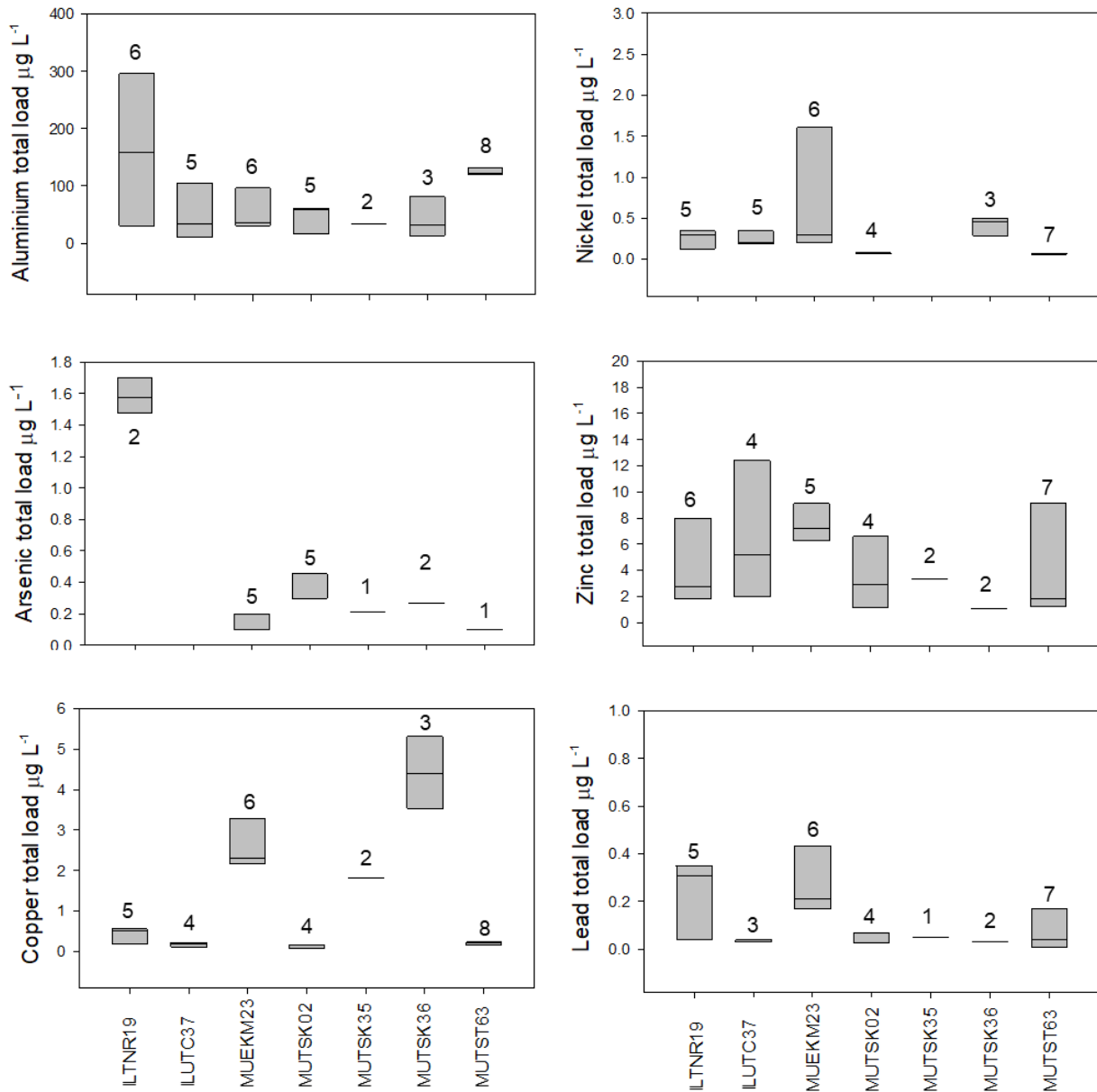


Figure 11. Box plots of trace metals in sediment samples for strategic sites. Box midline is median, box boundaries are 25th and 75th percentiles, box whiskers are 10th and 90th percentiles, and number above each box is the number of samples per site. Results below limit of detection were not included.

Comparison of trace metal concentrations in sediment and water suggests that elevated copper concentrations observed in waters from MUEKM23, MUTSK36 and MUTSK35 (only one sample) may relate to elevated concentrations in stream sediments.

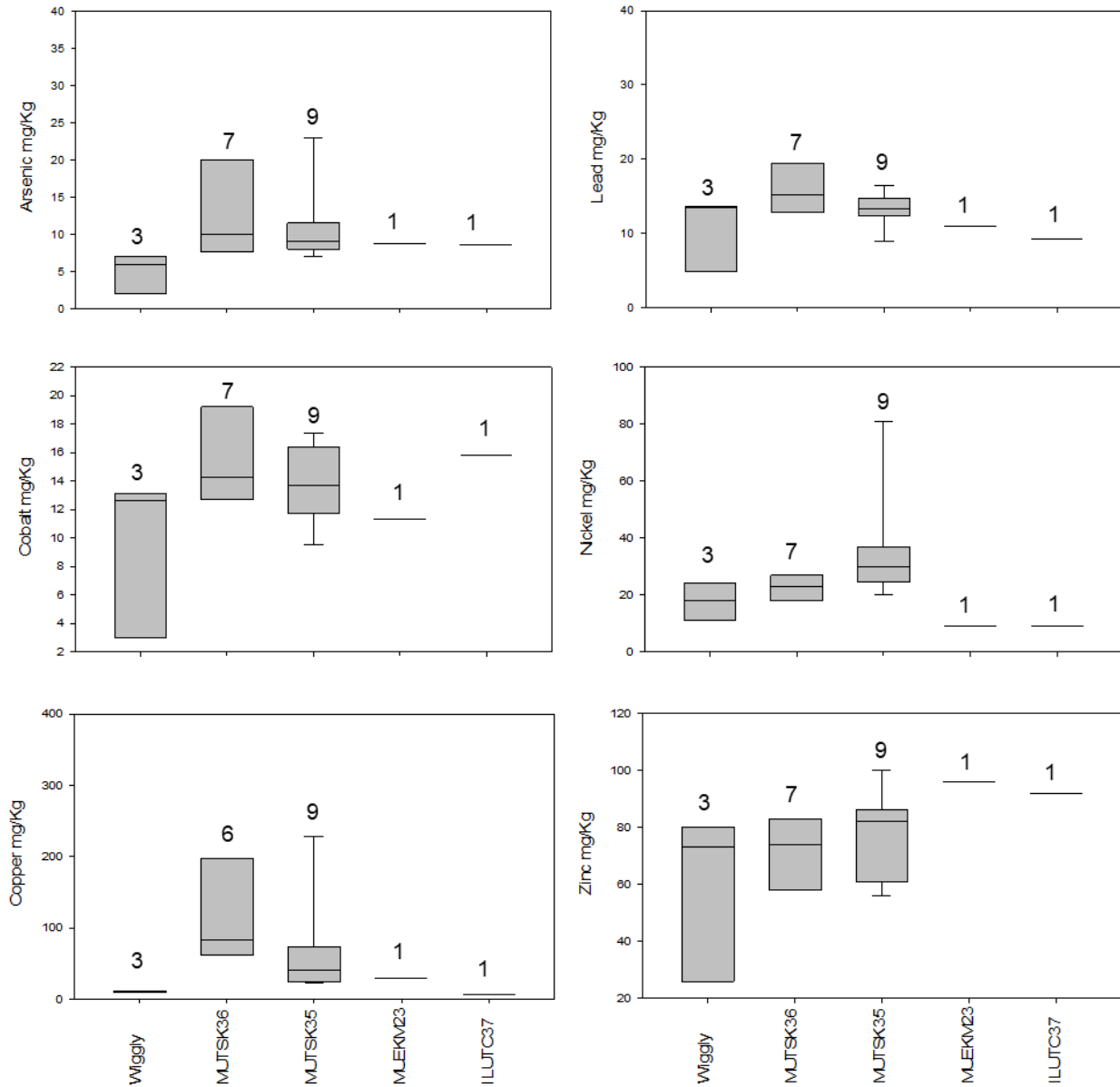


Figure 12. Box plots for trace metals in water analyzed for strategic sites. Box midline is median, box boundaries are 25th and 75th percentiles, box whiskers are 10th and 90th percentiles, and the number above each box is the number of samples per site. Field duplicate samples collected by TNC were included as individual samples in this graph. Results below limit of detection were not included.

5. Conclusions and future recommendations

This report analyzed water samples for major, minor and trace elements, collected in June 2015 from 40 wadeable streams (1st through 4th order) in the Nushagak and Kvichak River watersheds. All investigated streams of the study area are pristine with neutral pH, very low solute concentrations, and low buffer capacity (here analyzed as hardness).

Objective 1: Are there exceedances of water quality?

The low concentrations in hardness caused low hardness-dependent threshold values for respective elements. However, with the exception of zinc and barium, the number of exceedances above threshold levels were small even though a large number of metal concentrations in stream and lake sediments analyzed by the U.S. Geological Survey were above lower effect levels listed for freshwater sediments as listed in SQuiRTs. This indicates that, when undisturbed, high metal concentrations in sediments and respective source bedrock may not produce toxic metal concentrations in streams. However, increasing erosion due to changes in climate or other processes may release these elements to the aquatic environment in the future.

The low buffer capacity makes the streams highly susceptible to toxic metal concentrations should physico-chemical conditions change. An example is given by the tributary of the Stuyahok River sampled by TNC and also for this study (MUTSK63). Extremely low conductivity, reflected in low total solute concentrations of 2.2 mg L⁻¹ [Zamzow, 2011], and low pH values (pH 5.4) during one sample event resulted in very low acute and chronic threshold levels that resulted in exceedances for copper, lead, zinc, and aluminum. Low hardness directly decreases the threshold levels and therefore can increase the number of exceedances. In addition, low hardness can be accompanied by low pH values, which increases metal solubility in water and may also increase the number of exceedances.

In summary, exceedances were recorded for aluminum, barium, copper, lead, and zinc. Barium only revealed exceedances when applying the more stringent thresholds. Site MUTSK63 had a total of eight samples with exceedances (Al, Cu, Pb, and Zn) followed by MUEKM23 (5), MUTSK36 (4), ILTNR19 (2) and ILUT37 (1). The exceedances in zinc were only recorded in the data collected in this report and should be confirmed through additional sampling. Zinc was strongly correlated to aluminum, which peaked in May samples collected by TNC, indicating dust accumulated in snow as a possible source. For other elements, limited data precluded our ability to evaluate seasonality in exceedances.

Objective 2: How different are results across years at strategic sites?

Historic sampling by TNC at eight of our strategic sites provided some information on differences from year to year and between snowmelt in May and water quality concentrations in June. Some of the differences in aluminum concentrations can be explained by dust accumulation in snow as aluminum concentrations were highest in May. The correlation between aluminum and zinc further suggests that the high zinc values may also be attributed to accumulation of dust particles in snowmelt. Additional data collection during breakup is required to confirm this result.

Elevated concentrations of conservative (e.g. calcium) and trace elements (e.g. copper) during early summer baseflow suggest bedrock weathering as the predominant source. A better record of snowmelt versus summer baseflow is needed to confirm this assumption.

The differences in water chemistry of samples collected at different times of the year indicate seasonal differences in water chemistry. However, we want to highlight that the available data reviewed for this

report are not sufficient for assessing overall water quality and exceedances. Samples collected at different times of the year show differences in metal concentrations and consequently exceedances of chronic and acute threshold levels. Increased sampling across seasons and years will lead to a better understanding of the linkages between environmental setting, climate and water chemistry.

Objective 3: What is the distribution of parameter concentrations across small and large wadable streams in the study area?

Water quality characteristics were generally similar across large and small streams with a few exceptions. However, additional sampling could be used to confirm whether these differences hold for other seasons and from year to year.

Objective 4: Do the data indicate locations of potential mineralization in the study area?

The streams sampled in this report did not indicate specific mineralization in the study area. However, together with data collected by TNC, elevated copper concentrations in both water and sediments in three watersheds (MUEKM23, MUTSK36, and MUTSK35) indicate mineralization. These watersheds cluster around the Pebble porphyry copper, gold, and molybdenum mineral deposit. As discussed above these are preliminary conclusions that require further investigation.

Future Recommendations

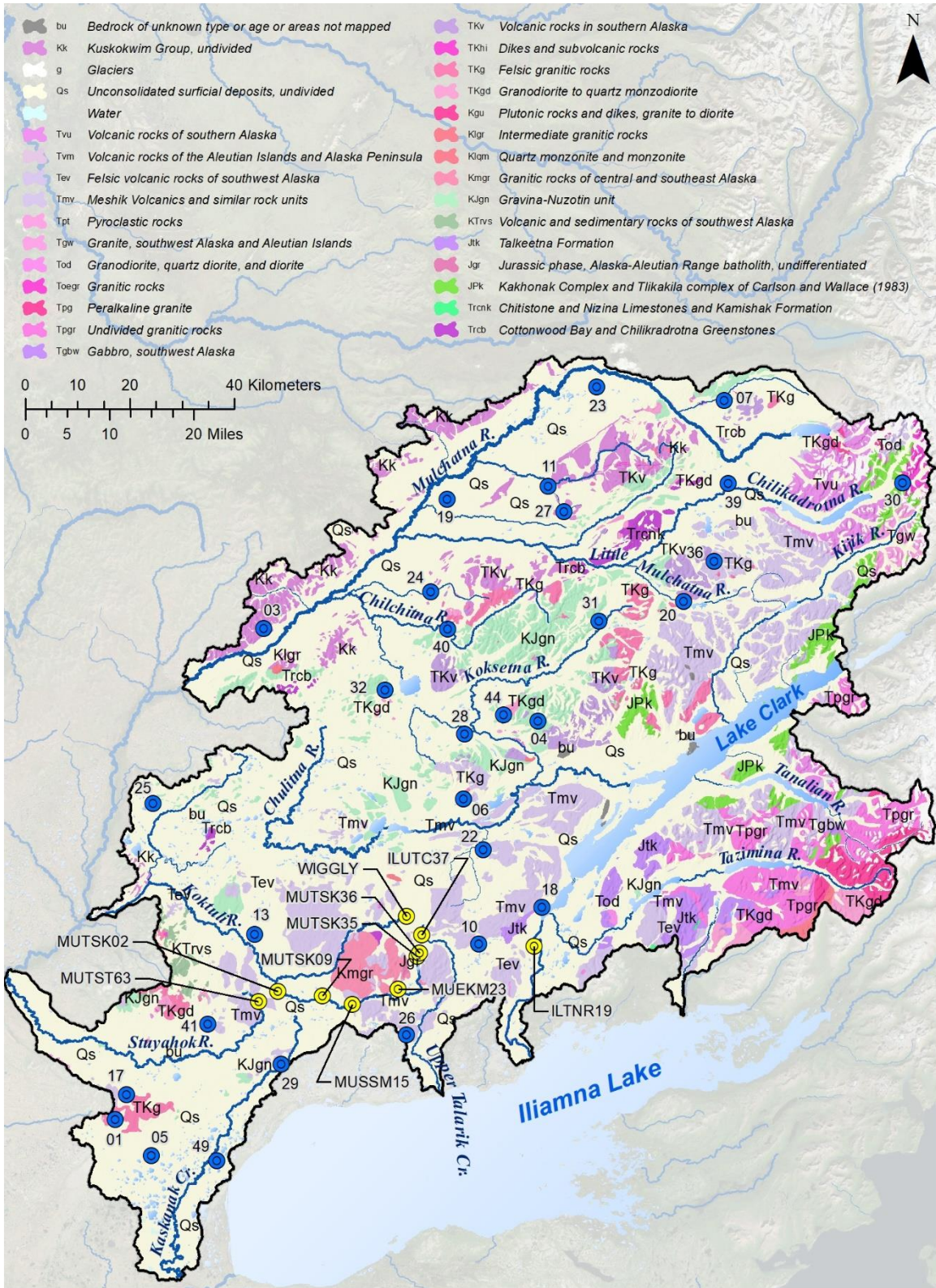
This study provided an overview of the water chemistry of wadeable streams in the Lime Hills ecoregion of Bristol Bay but only for one year and one season. A large dataset exists, but these data are not publicly available and cannot be used. We recommend additional sampling of stream water chemistry in this area given its highly productive salmon fisheries and its susceptibility to both climate change and resource development.

- 1) We recommend sampling over additional seasons and years to fully detect and understand metal concentrations in the different systems. Sampling over multiple seasons would provide better information on chemical transport and also verify some of the high metal levels found in our dataset and in the TNC dataset. Capturing the full variation of metal concentrations across seasons and from year to year is important for fully describing the water chemistry regime for wadeable streams of Bristol Bay.
- 2) Additional water samples should be analyzed for a complete water chemistry suite that includes metals, cations, anions, hardness, DOC, DIC, and in-situ parameters. This would enable chemical equilibrium modeling that can be used to determine metal speciation, which affects the bioavailability of metals to aquatic organisms. It would also allow for proper calculation of acute and chronic threshold levels that are dependent on more than hardness- or DOC- such as barium [Golding *et al.*, 2018].
- 3) Water quality sampling should be conducted in reference sites and in sites downstream of mineralizations to measure trends in water quality, seasonality, and potential impacts from climate change. Important streams for monitoring include the North and South Fork Koktuli mainstem channels and their tributaries, including the strategically-selected sites in this study that indicated mineralization. A larger dataset would allow for understanding effects from seasonality, mineralization or changes in climate. For example, climate change could be altering stream nutrients and thermal regimes and also metal speciation that can affect their bioavailability, which is relevant for sustainable food resources.

1 References

- ADEC (2003), Alaska Water Quality Criteria for Toxic and other Deleterious and Inorganic Substances, edited by A. D. o. E. Conservation, Alaska Department of Environmental Conservation.
- Anderson, S. P., and A. E. Blum (2003), Controls on chemical weathering: small- and large-scale perspectives, *Chemical Geology*, 202(3-4), 191-193.
- Buchman, M. (2008), Screening Quick Reference Tables (SQiRTs).
- Buchman, M. F. (1999), NOAA Screening Quick Reference Tables *Rep.*, 12 pp, Coastal Protection and Restoration Division, Seattle, WA.
- Caissie, D. (2006), The thermal regime of rivers: a review., *Freshwater Biology*, 51, 1389-1406.
- EPA (2007), in https://www.epa.gov/sites/production/files/2015-06/documents/wi_337_04032007.pdf, edited by E. P. Agency.
- EPA (2014), An Assessment of Potential Mining Impacts on Salmon Ecosystems of Bristol Bay, Alaska. Region 10. *Rep.*, Seattle, WA.
- EPA (2018), Final Aquatic Life Ambient Water Quality Criteria For Aluminium 2018 *Rep.*, 329 pp.
- Golding, L. A., K. McKnight, M. Binet, M. Adams, and S. C. Apte (2018), Toxicity of dissolved and precipitated forms of barium to a freshwater alga (*Chlorella* sp. 12) and water flea (*Ceriodaphnia dubia*), *Environmental Toxicology and Chemistry*, 37(6), 1632-1642, doi:10.1002/etc.4107.
- Hogstrand, C. (2011), Homeostasis and toxicology of essential metals zinc, *Homeostasis and toxicology of essential metals*, 135-200.
- Kincaid, T. M., Olsen, A. R., and Weber, M. H. (2019). spsurvey: Spatial Survey Design and Analysis. R package version 4.1.0.
- Knapp, G. M., M. GUettabi, and S. Goldsmith (2013), The Economic Importance of the Bristol Bay Salmon Industry *Rep.*, Institute of Social and Economic Research, UNiversity of Alaska Anchorage.
- R Core Team (2019). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <https://www.R-project.org/>.
- Stumm, W., and J. J. Morgan (1996), *Aquatic Chemistry*, 3 ed., 1022 pp., John Wiley & Sons, INC, New York, Chichester, Brisbane, Toronto, Singapore.
- Wilson F.H., C. P. Hulst, C. G. Mull, and S. M. Karl (2015), Geologic Map of Alaska: U.S. Geological Survey Scientific Investigations Map 3340, U.S. Geological Survey, U.S. Geological Survey, Reston, Virginia.
- Zamzow, K. L. (2011), Surface water quality near the Pebble Prospect, southwest Alaska, 2009 - 2010 *Rep.*, 43 pp, The Nature Conservancy, Anchorage, AK.

2 Appendices



Appendix 1. Geologic map of study area with sampling sites from 2015.

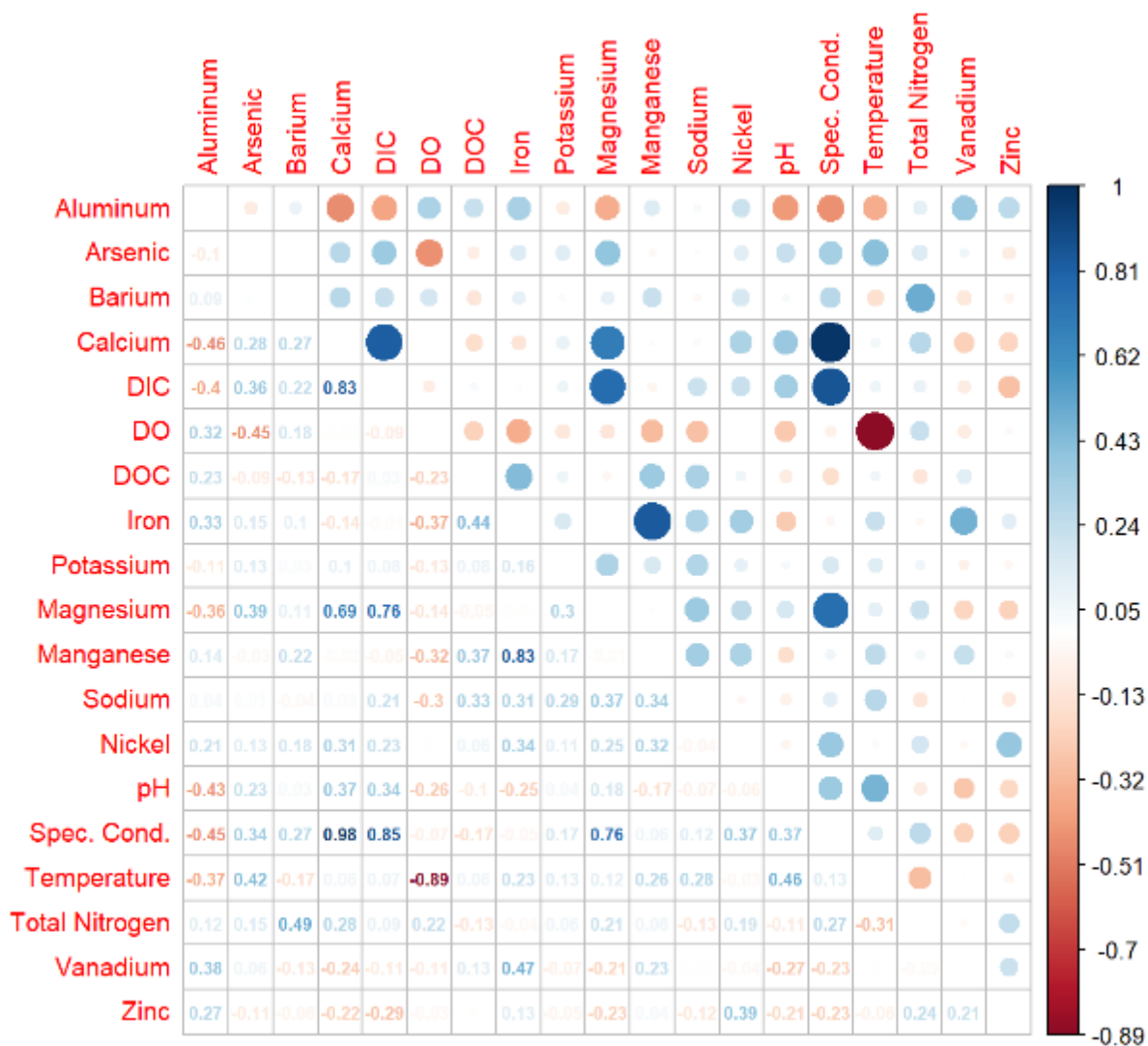
Appendix 2. Cumulative distribution functions for 31 water quality parameters for small, large, and all streams included in the probabilistic survey design. (Provided in a separate document.)

Appendix 3. In situ water quality and chemical analyses results on the ACCS Data Catalog entry for Bristol Bay Monitoring Data (<https://accscatalog.uaa.alaska.edu/dataset/bristol-bay-monitoring-data>).

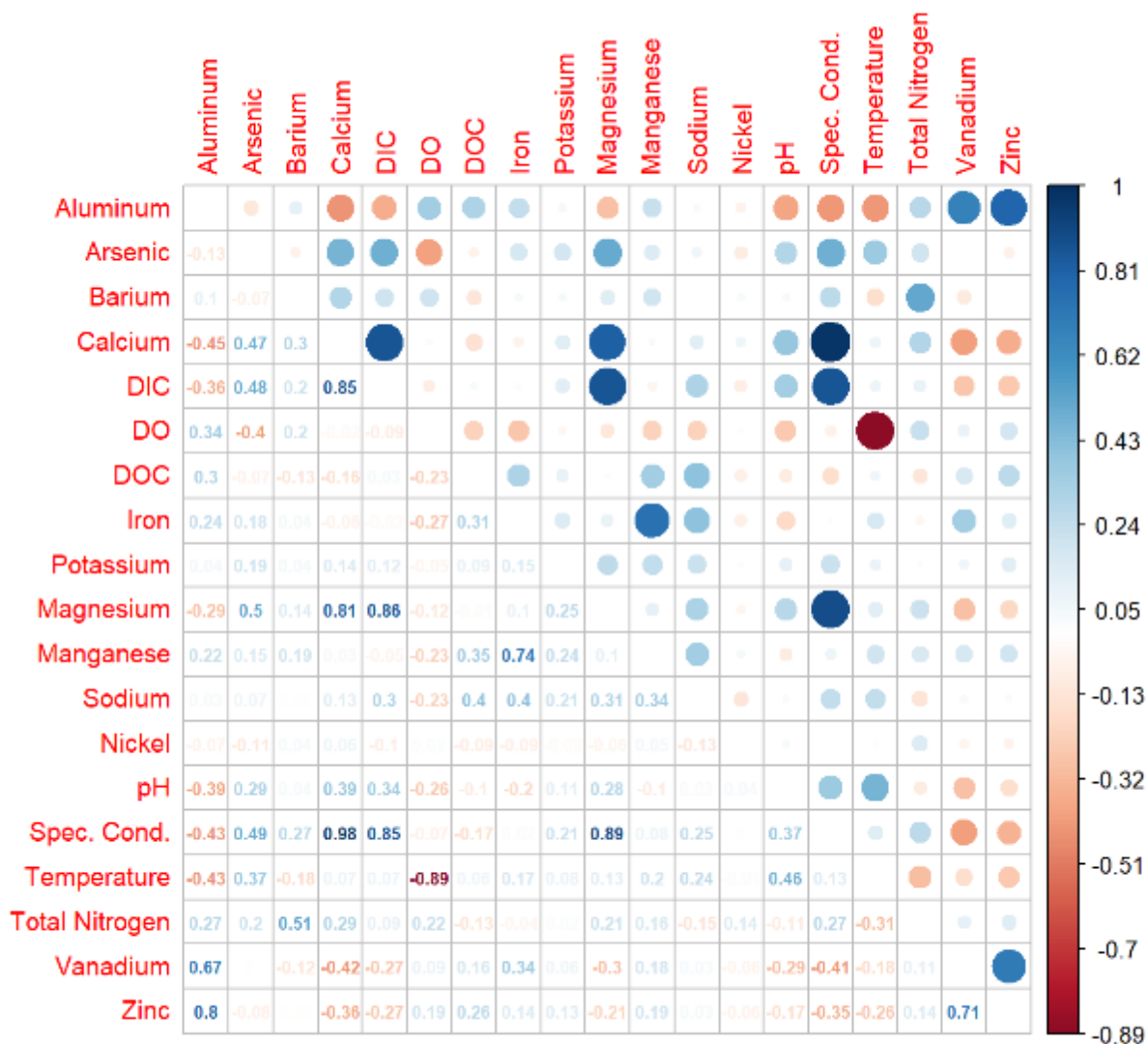
Appendix 4. Summary statistics for water quality parameters analyzed in 40 sampling sites in 2015. Means are shown for four different populations with standard deviations in parentheses. All streams include all 30 randomly-selected sampling sites. Small streams include 12 randomly-selected first and second order streams. Large streams include 18 randomly-selected third and fourth order streams. Strategic streams include ten strategically-selected streams in the southwest portion of the study area. For 25 parameters, more than 50% of the results were below method detection limits and were not included in this table. Results below method detection limits for the remaining parameters were replaced with half the method detection limit for this table.

Group	Parameter	Units	All streams	Small streams	Large streams	Strategic streams
In Situ Parameters	Alkalinity	mg/L CaCo3	22.42 (10.21)	19.37 (9.05)	26.17 (10.31)	18.68 (11.26)
In Situ Parameters	Dissolved oxygen	mg/L	11.72 (1.22)	11.84 (1.15)	11.51 (1.31)	11.21 (0.86)
In Situ Parameters	pH	NA	7.31 (0.25)	7.27 (0.24)	7.37 (0.24)	7.19 (0.38)
In Situ Parameters	Specific conductance	µS/cm	59.7 (27.2)	56.33 (23.77)	65.64 (31.5)	56.64 (29.52)
In Situ Parameters	Temperature	°C	8.14 (3.96)	7.49 (3.09)	9.28 (4.93)	12.34 (4.21)
Major Ions	Ca	ug/L	7693.31 (3999.32)	7290.02 (3647.92)	8403.1 (4464.75)	6692.03 (3504.56)
Major Ions	Ca dissolved	ug/L	6733.25 (3605.34)	6386.05 (3227.94)	7344.32 (4117.26)	5957.08 (3117.05)
Major Ions	K	ug/L	372.32 (217.28)	354.61 (249.33)	403.49 (139.19)	320.69 (160.11)
Major Ions	K dissolved	ug/L	374.3 (219.11)	363.73 (253.34)	392.89 (137.87)	321.69 (162.91)
Major Ions	Mg	ug/L	1542.63 (839.43)	1419.89 (568.7)	1758.65 (1141.24)	1438.58 (1067.2)
Major Ions	Mg dissolved	ug/L	1515.34 (849.47)	1409.55 (614.23)	1701.54 (1128.37)	1485.28 (1119.14)
Major Ions	Na	ug/L	2317.01 (646.71)	2360.7 (739.41)	2240.11 (427.57)	2451.03 (918.41)
Major Ions	Na dissolved	ug/L	2191.43 (612.37)	2241.88 (682.49)	2102.64 (450.37)	2413.7 (946.29)
Metals	Al	ug/L	37.57 (44.9)	30.56 (29.66)	49.91 (61.46)	16.37 (11.87)
Metals	Al dissolved	ug/L	16.51 (14.02)	17.87 (15.67)	14.11 (10.08)	10.81 (6.69)
Metals	As	ug/L	0.59 (0.66)	0.34 (0.29)	1.01 (0.88)	0.33 (0.48)
Metals	Ba	ug/L	5.09 (6.27)	5.02 (7.52)	5.21 (2.99)	4 (2.45)
Metals	Ba dissolved	ug/L	4.56 (5.71)	4.54 (6.82)	4.59 (2.88)	3.54 (2.27)
Metals	Fe dissolved	ug/L	96.31 (105.67)	96.93 (104.71)	95.21 (107.35)	105.36 (119.29)
Metals	Mn	ug/L	2.4 (3.86)	1.6 (1.82)	3.82 (5.68)	3.04 (3.48)
Metals	Mn dissolved	ug/L	7.44 (8.81)	7.11 (8.95)	8.03 (8.54)	13.5 (16.99)

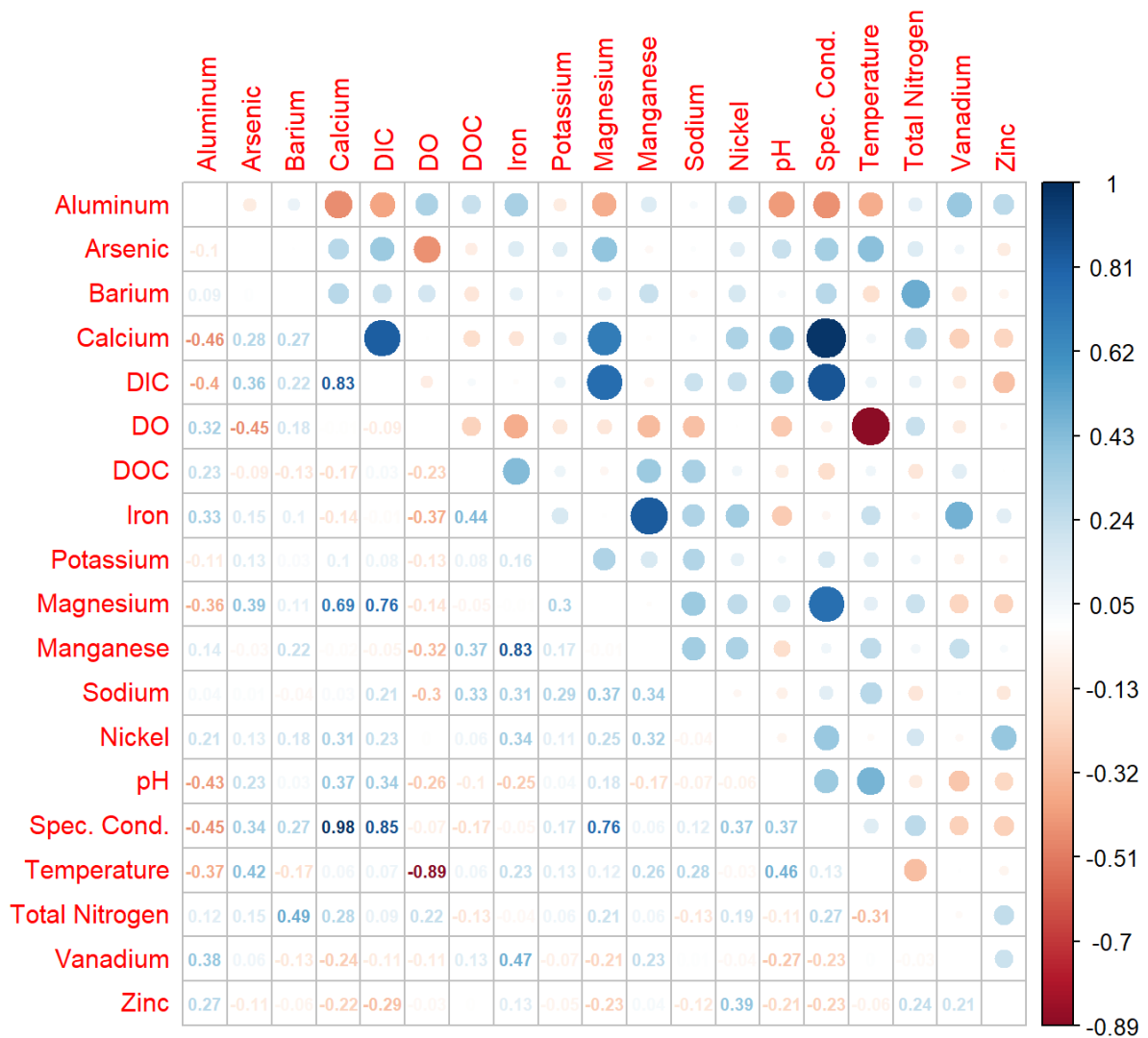
Group	Parameter	Units	All streams	Small streams	Large streams	Strategic streams
Metals	Mo	ug/L	0.23 (0.3)	0.17 (0.13)	0.32 (0.46)	0.63 (0.94)
Group	Parameter	Units	All streams	Small streams	Large streams	Strategic streams
Metals	Ni dissolved	ug/L	0.2 (0.09)	0.21 (0.09)	0.18 (0.08)	0.17 (0.14)
Metals	Sb	ug/L	1.4 (0.28)	1.39 (0.19)	1.41 (0.38)	1.4 (0.32)
Metals	Si	ug/L	5077.42 (1495.29)	5182.45 (1563.83)	4892.55 (1346.56)	5269.96 (1460.5)
Metals	V	ug/L	0.47 (0.31)	0.44 (0.25)	0.51 (0.38)	0.41 (0.26)
Metals	V dissolved	ug/L	0.31 (0.22)	0.34 (0.2)	0.25 (0.23)	0.35 (0.27)
Metals	Zn	ug/L	1149.71 (1672.76)	917.84 (1564.02)	1557.79 (1776.63)	282.36 (681.22)
Nutrients	DIC	mg/L	6.08 (2.04)	5.99 (1.89)	6.24 (2.27)	5.06 (2.73)
Nutrients	DOC	mg/L	3.93 (4.7)	4.88 (5.62)	2.26 (1.03)	2.01 (0.97)
Nutrients	TN	mg/L	0.21 (0.15)	0.21 (0.16)	0.21 (0.14)	0.14 (0.11)



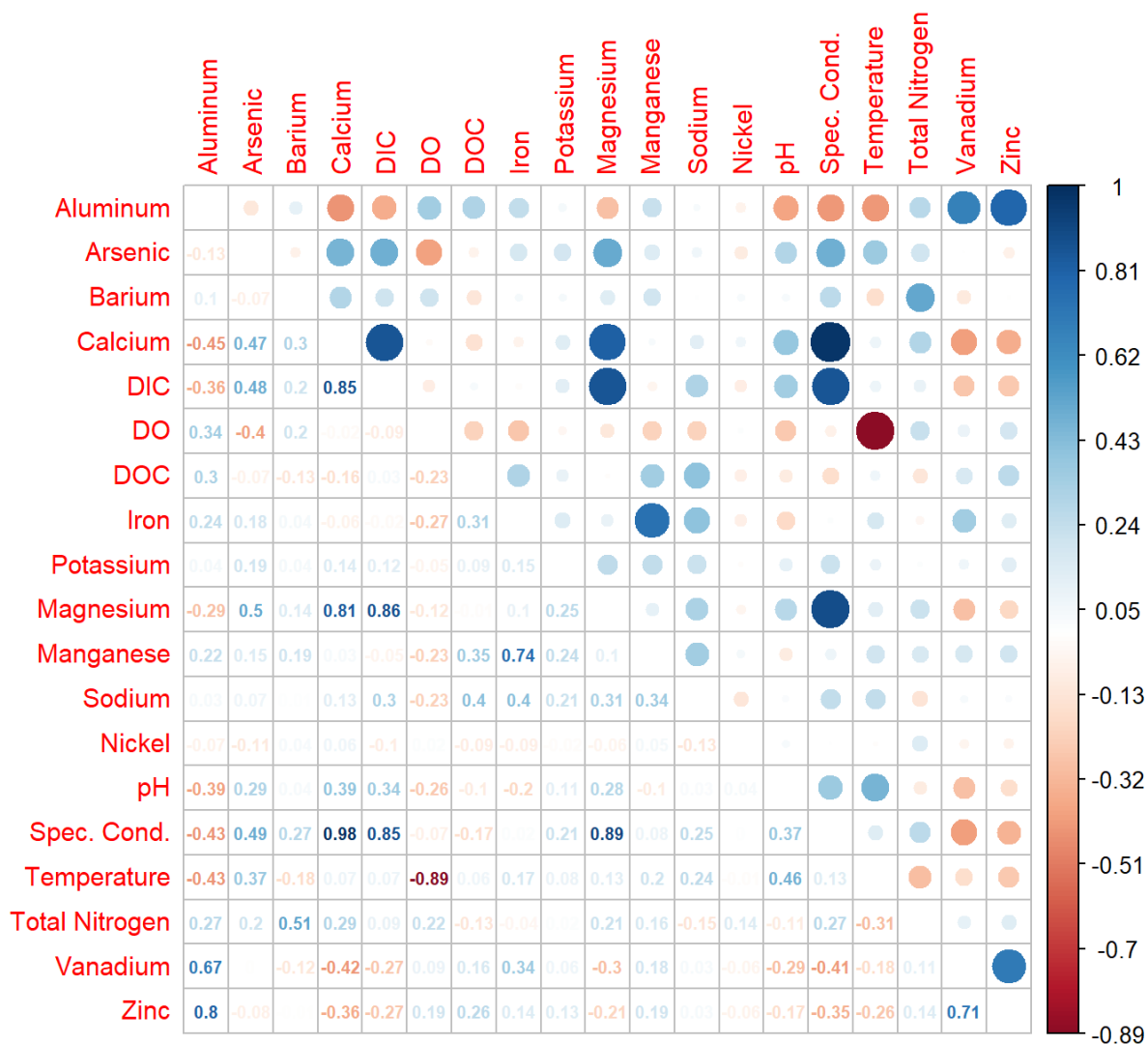
Appendix 5. Correlation between dissolved load and water quality parameters for 2015 sampling data.



Appendix 6. Correlation between total load and water quality parameters for 2015 sampling data.



Appendix 7. Correlation between dissolved load and water quality parameters for all strategic sites, including TNC samples.



Appendix 8. Correlation between total load and water quality parameters for all strategic sites, including TNC samples.

Appendix 9. Acute and chronic threshold levels for hardness-dependent parameters for dissolved load; based on hardness (1) as CaCO₃.

SITE_ID	Watershed	Hardness as CaCO ₃ ppm	Cd		Cr (III)		Cu		Pb		Ni		Zn	
			AC	CR	AC	CR	AC	CR	AC	CR	AC	CR	AC	CR
AKBB-001	Trib to Kaskanak Cr	5.76	0.12	0.03	55.33	7.20	0.91	0.78	2.60	0.03	41.85	4.60	10.52	10.43
AKBB-003	Trib to Mulchatna R	58.63	1.20	0.17	367.96	47.86	8.13	5.68	35.95	1.40	298.06	32.56	75.15	74.54
AKBB-004	Trib to Koksetna R	59.03	1.21	0.17	369.99	48.13	8.18	5.71	36.22	1.41	299.76	32.75	75.58	74.97
AKBB-005	Trib to Kaskanak Cr	11.73	0.25	0.06	98.50	12.81	1.78	1.43	5.89	0.11	76.40	8.38	19.22	19.07
AKBB-006	Trib to Chulitna R	19.57	0.41	0.08	149.78	19.48	2.89	2.22	10.53	0.25	117.79	12.90	29.66	29.42
AKBB-007	Trib to Mulchatna R	11.36	0.24	0.05	95.93	12.48	1.73	1.40	5.67	0.10	74.34	8.16	18.70	18.55
AKBB-010	Trib to Steambath Cr	33.77	0.70	0.12	234.19	30.46	4.83	3.54	19.46	0.60	186.90	20.45	47.09	46.71
AKBB-011	Victoria Creek	34.55	0.72	0.12	238.60	31.04	4.94	3.61	19.96	0.62	190.53	20.84	48.01	47.62
AKBB-013	Trib to Koktuli R	11.59	0.25	0.05	97.53	12.69	1.76	1.42	5.81	0.11	75.62	8.30	19.03	18.87
AKBB-017	Trib to Stuyahok R	5.98	0.13	0.03	56.70	7.38	0.95	0.81	2.72	0.03	43.19	4.75	10.86	10.77
AKBB-018	Trib to 6 Mile Lake	14.44	0.31	0.06	116.78	15.19	2.17	1.71	7.46	0.15	91.09	9.99	22.92	22.74
AKBB-019	Trib to Mulchatna R	28.94	0.60	0.10	206.40	26.85	4.18	3.10	16.37	0.47	164.04	17.95	41.32	40.99
AKBB-020	Little Mulchatna River	22.17	0.46	0.09	165.92	21.58	3.25	2.47	12.12	0.31	130.92	14.34	32.97	32.70
AKBB-022	Trib to Rock Cr	18.13	0.38	0.07	140.73	18.31	2.69	2.08	9.66	0.22	110.44	12.10	27.80	27.58
AKBB-023	Trib to Mulchatna R	43.30	0.89	0.14	287.08	37.34	6.11	4.38	25.68	0.88	230.65	25.22	58.13	57.66
AKBB-024	Dummy Creek	20.15	0.42	0.08	153.39	19.95	2.97	2.28	10.88	0.26	120.72	13.23	30.40	30.15
AKBB-025	North Fork Swan River	27.48	0.57	0.10	197.81	25.73	3.98	2.97	15.44	0.43	156.99	17.18	39.54	39.22
AKBB-026	Trib to Upper Talarik Cr	20.72	0.43	0.08	156.98	20.42	3.05	2.33	11.23	0.28	123.64	13.54	31.13	30.88
AKBB-027	Victoria Creek	36.07	0.75	0.12	247.15	32.15	5.14	3.75	20.94	0.66	197.59	21.61	49.79	49.38
AKBB-028	Trib to Koksetna R	18.02	0.38	0.07	140.03	18.21	2.67	2.07	9.59	0.22	109.87	12.04	27.66	27.44
AKBB-029	Kaskanak Creek	15.57	0.33	0.07	124.24	16.16	2.33	1.83	8.13	0.17	97.10	10.64	24.44	24.24
AKBB-030	Trib to Twin Lakes	17.96	0.38	0.07	139.63	18.16	2.67	2.07	9.55	0.22	109.55	12.01	27.58	27.36

SITE_ID	Watershed	Hardness as CaCO3 ppm	Cd		Cr (III)		Cu		Pb		Ni		Zn	
			AC	CR	AC	CR	AC	CR	AC	CR	AC	CR	AC	CR
AKBB-031	Headwater Trib to Ko	24.08	0.50	0.09	177.53	23.09	3.51	2.65	13.31	0.35	140.39	15.37	35.36	35.07
AKBB-032	Trib to Tutna Lake	22.80	0.48	0.09	169.74	22.08	3.34	2.53	12.51	0.32	134.03	14.68	33.75	33.48
AKBB-036	Trib to Chilikadrotna R	24.90	0.52	0.09	182.48	23.74	3.63	2.73	13.82	0.37	144.44	15.82	36.38	36.08
AKBB-039	Trib to Chilikadrotna R	29.69	0.62	0.11	210.77	27.42	4.28	3.17	16.85	0.49	167.62	18.35	42.23	41.88
AKBB-040	Chilchitna River	34.60	0.72	0.12	238.90	31.08	4.94	3.62	20.00	0.62	190.78	20.87	48.07	47.68
AKBB-041	Trib to Stuyahok R	9.28	0.20	0.05	81.30	10.58	1.43	1.17	4.50	0.07	62.66	6.88	15.76	15.63
AKBB-044	Trib to Koksetna R	17.77	0.37	0.07	138.41	18.00	2.64	2.05	9.44	0.22	108.56	11.90	27.33	27.11
AKBB-049	Trib to Kaskanak Cr	19.59	0.41	0.08	149.91	19.50	2.89	2.22	10.54	0.25	117.89	12.92	29.68	29.44
ILTNR19	Steambath Creek	25.23	0.53	0.09	184.42	23.99	3.67	2.76	14.02	0.38	146.03	15.99	36.78	36.48
ILUTC37	Upper Talarik Creek	40.07	0.83	0.13	269.39	35.04	5.68	4.10	23.56	0.78	215.99	23.62	54.43	53.99
MUEKM23	Trib to SF Kaktuli R	21.15	0.44	0.08	159.64	20.77	3.11	2.37	11.50	0.29	125.80	13.78	31.68	31.42
MUTST63	Trib to SF Kaktuli R	7.55	0.16	0.04	68.67	8.93	1.18	0.98	3.56	0.05	52.63	5.78	13.23	13.13
MUSSM15	Trib to SF Kaktuli R	15.31	0.32	0.07	122.50	15.93	2.29	1.80	7.97	0.17	95.70	10.49	24.09	23.89
MUTSK02	Trib to SF Kaktuli R	12.21	0.26	0.06	101.81	13.24	1.85	1.49	6.16	0.12	79.05	8.67	19.89	19.73
MUTSK09	Trib to SF Kaktuli R	13.87	0.29	0.06	112.97	14.69	2.09	1.66	7.12	0.14	88.01	9.65	22.15	21.97
MUTSK35	Trib to Stuyahok R	31.01	0.64	0.11	218.41	28.41	4.46	3.29	17.69	0.52	173.90	19.03	43.81	43.46
MUTSK36	Trib to NF Kaktuli R	22.62	0.47	0.09	168.69	21.94	3.31	2.52	12.40	0.32	133.18	14.59	33.54	33.26
WIGGLY	Trib to NF Kaktuli R	21.82	0.46	0.09	163.75	21.30	3.20	2.44	11.91	0.30	129.15	14.15	32.52	32.26

Appendix 10. Acute and chronic threshold levels for hardness-dependent parameters for total load; based on hardness (1) as CaCO₃.

Sample ID	Location	Hardness as CaCO ₃ ppm	Cd		Cr (III)		Cu		Pb		Ni		Zn	
			AC	CR	AC	CR	AC	CR	AC	CR	AC	CR	AC	CR
AKBB-001	Trib to Kaskanak Cr	6.53	0.13	0.14	192.86	2.79	1.07	0.91	2.53	0.10	46.62	5.14	11.86	11.86
AKBB-003	Trib to Mulchatna R	61.00	1.29	1.25	1202.80	4.19	8.79	6.12	43.52	1.70	308.83	34.03	78.82	78.82
AKBB-004	Trib to Koksetna R	65.92	1.40	1.34	1281.72	4.25	9.45	6.53	48.03	1.87	329.79	36.34	84.17	84.17
AKBB-005	Trib to Kaskanak Cr	12.87	0.27	0.27	336.28	3.16	2.03	1.62	6.00	0.23	82.79	9.12	21.09	21.09
AKBB-006	Trib to Chulitna R	19.87	0.41	0.42	480.00	3.42	3.05	2.35	10.44	0.41	119.57	13.17	30.47	30.47
AKBB-007	Trib to Mulchatna R	12.74	0.26	0.27	333.47	3.15	2.01	1.60	5.92	0.23	82.08	9.04	20.90	20.90
AKBB-010	Trib to Steambath Cr	39.04	0.82	0.81	834.56	3.86	5.77	4.18	24.66	0.96	211.72	23.33	54.00	54.00
AKBB-011	Victoria Creek	36.97	0.78	0.76	798.14	3.82	5.48	3.99	23.00	0.90	202.18	22.28	51.57	51.57
AKBB-013	Trib to Koktuli R	12.61	0.26	0.27	330.66	3.14	1.99	1.59	5.85	0.23	81.36	8.97	20.72	20.72
AKBB-017	Trib to Stuyahok R	6.79	0.15	0.15	199.31	2.81	1.11	0.94	2.66	0.10	48.23	5.31	12.27	12.27
AKBB-018	Trib to 6 Mile Lake	15.72	0.33	0.33	396.20	3.27	2.45	1.92	7.75	0.30	98.07	10.81	24.99	24.99
AKBB-019	Trib to Mulchatna R	32.47	0.68	0.67	717.59	3.74	4.85	3.57	19.50	0.76	181.14	19.96	46.19	46.19
AKBB-020	Little Mulchatna River	23.66	0.49	0.49	553.86	3.53	3.60	2.72	13.04	0.51	138.62	15.27	35.33	35.33
AKBB-022	Trib to Rock Cr	20.16	0.42	0.42	485.63	3.43	3.10	2.37	10.63	0.41	121.02	13.33	30.84	30.84
AKBB-023	Trib to Mulchatna R	45.11	0.95	0.93	939.45	3.97	6.61	4.73	29.64	1.15	239.26	26.36	61.04	61.04
AKBB-024	Dummy Creek	21.27	0.45	0.45	507.47	3.46	3.26	2.49	11.38	0.44	126.64	13.95	32.28	32.28
AKBB-025	North Fork Swan River	31.16	0.65	0.65	693.81	3.71	4.67	3.44	18.50	0.72	174.94	19.28	44.61	44.61
AKBB-026	Trib to Upper Talarik Cr	22.99	0.48	0.48	540.80	3.51	3.50	2.66	12.56	0.49	135.25	14.90	34.47	34.47
AKBB-027	Victoria Creek	39.72	0.83	0.82	846.47	3.87	5.87	4.24	25.21	0.98	214.84	23.67	54.80	54.80
AKBB-028	Trib to Koksetna R	30.05	0.63	0.62	673.60	3.68	4.51	3.34	17.67	0.69	169.68	18.70	43.26	43.26
AKBB-029	Kaskanak Creek	17.82	0.37	0.38	439.08	3.35	2.76	2.14	9.09	0.35	109.06	12.02	27.79	27.79
AKBB-030	Trib to Twin Lakes	20.07	0.42	0.42	483.87	3.42	3.08	2.36	10.57	0.41	120.57	13.28	30.73	30.73

Sample ID	Location	Hardness as CaCO ₃ ppm	Cd		Cr (III)		Cu		Pb		Ni		Zn	
			AC	CR	AC	CR	AC	CR	AC	CR	AC	CR	AC	CR
AKBB-031	Headwater Trib to Ko	25.94	0.54	0.54	597.09	3.59	3.93	2.94	14.65	0.57	149.81	16.51	38.19	38.19
AKBB-032	Trib to Tutna Lake	26.35	0.55	0.55	604.91	3.60	3.99	2.99	14.95	0.58	151.84	16.73	38.71	38.71
AKBB-036	Trib to Chilikadrotna R	27.04	0.56	0.56	617.75	3.61	4.08	3.05	15.45	0.60	155.17	17.10	39.56	39.56
AKBB-039	Trib to Chilikadrotna R	33.43	0.70	0.69	734.99	3.76	4.99	3.66	20.24	0.79	185.68	20.46	47.35	47.35
AKBB-040	Chilchitna River	37.46	0.79	0.77	806.86	3.83	5.55	4.03	23.40	0.91	204.46	22.53	52.15	52.15
AKBB-041	Trib to Stuyahok R	10.41	0.22	0.22	282.66	3.04	1.66	1.35	4.58	0.18	69.19	7.62	17.62	17.62
AKBB-044	Trib to Koksetna R	19.83	0.42	0.42	479.24	3.42	3.05	2.34	10.41	0.41	119.37	13.15	30.42	30.42
AKBB-049	Trib to Kaskanak Cr	22.12	0.46	0.46	524.05	3.48	3.38	2.57	11.96	0.47	130.92	14.43	33.37	33.37
ILTNR19	Steambath Creek	29.04	0.61	0.60	654.97	3.66	4.37	3.24	16.92	0.66	164.83	18.16	42.03	42.03
ILUTC37	Upper Talarik Creek	42.68	0.90	0.88	897.85	3.93	6.28	4.51	27.62	1.08	228.32	25.16	58.24	58.24
MUEKM23	Trib to SF Kaktuli R	23.95	0.50	0.50	559.34	3.53	3.64	2.75	13.24	0.52	140.04	15.43	35.70	35.70
MUTST63	Trib to SF Kaktuli R	6.43	0.14	0.14	190.50	2.78	1.05	0.89	2.48	0.10	46.03	5.07	11.71	11.71
MUSSM15	Trib to SF Kaktuli R	16.23	0.34	0.34	406.73	3.29	2.52	1.97	8.07	0.31	100.77	11.10	25.67	25.67
MUTSK02	Trib to SF Kaktuli R	16.28	0.34	0.34	407.81	3.29	2.53	1.98	8.10	0.32	101.04	11.13	25.74	25.74
MUTSK09	Trib to SF Kaktuli R	5.16	0.11	0.11	159.06	2.67	0.86	0.74	1.87	0.07	38.20	4.21	9.72	9.72
MUTSK35	Trib to Stuyahok R	33.90	0.71	0.70	743.35	3.76	5.05	3.70	20.60	0.80	187.86	20.70	47.91	47.91
MUTSK36	Trib to NF Kaktuli R	30.15	0.63	0.63	675.29	3.69	4.52	3.35	17.74	0.69	170.12	18.74	43.38	43.38
WIGGLY	Trib to NF Kaktuli R	24.19	0.50	0.51	563.86	3.54	3.68	2.77	13.40	0.52	141.21	15.56	35.99	35.99