SURFACE WATER QUALITY NEAR THE PEBBLE PROSPECT,
SOUTHWEST ALASKA, 2009-2010

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for

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Executive Summary

This report summarizes a water quality data set collected near and within the Pebble Project area, Bristol Bay, Alaska, during 2009 and 2010. Data was collected both to verify Pebble Limited Partnership (PLP) surface water quality results and to sample streams outside the PLP study area. Data were collected at 14 surface water locations in May 2009, 22 locations in June 2009, and 18 locations in June 2010. A total of 31 different sampling locations were part of this study.

To confirm PLP water quality environmental baseline data collected since 2004, seven sites were co-located with PLP sites. Co-located sites were on the North Fork Koktuli River, South Fork Koktuli River, Upper Talarik Creek, and Kaskanak Creek. Other streams that were sampled north of the PLP study area include a tributary of the Chulitna River, a tributary of the Newhalen River, Groundhog Creek and Rock Creek. The Stuyahok River southwest of the PLP area was also sampled at three different locations. Field parameters were collected and surface water quality samples were analyzed in a fixed-base laboratory for a total of 33 constituents. Collection of surface water samples occurred during and after ice breakup to capture a range of water chemistry conditions in areas near and downstream of the Pebble deposit.

Results of this study confirmed that surface waters sampled in the PLP area were cold, well oxygenated, and had low concentrations of dissolved solutes, including metals. Metal concentrations, including dissolved metals, increased slightly during the May breakup sampling event. By June when stream discharge significantly decreased after breakup, metals concentrations at virtually all sample sites were below levels known to adversely affect freshwater aquatic life and were generally below analytical detection levels.

Most of the waters sampled were calcium-bicarbonate dominant, but low in alkalinity and hardness. Alkalinity and pH were strongly correlated with cation concentrations, primarily calcium, and with metals. When alkalinity and pH values decreased, metal concentrations generally increased, which occurred during spring breakup. Surface water quality in and around the PLP area had very low concentrations of metals and was low in parameters that can moderate metal toxicity, such as alkalinity, hardness and dissolved organic carbon.

Water chemistry within the PLP area appears to be influenced by both groundwater and surface runoff. The PLP water quality data reviewed for this study reported that certain stream reaches along the South Fork Koktuli River completely dry up during the summer low flow periods. This is attributed to inter-basin transfer of groundwater between two different watersheds, the South Fork Koktuli River (Nushagak) and Upper Talarik Creek (Kvichak). For this study, the degree of change in concentrations of calcium and other parameters was used to evaluate streams that may be influenced by groundwater from those primarily fed by surface runoff.

This study had a limited scope, but did support the findings of the baseline water quality data collected by the PLP. It also showed variation in water quality both between and within years— water quality associated with breakup differed from subsequent lower flow periods. This study also contributed to our understanding of water quality in streams outside the Pebble area that had not been sampled before. This study was part of a larger effort by The Nature Conservancy to investigate physical, biological, and chemical parameters at co-located sites, including water quality, algae, diatoms, macroinvertebrates and fish to better understanding watershed ecology in the headwaters of Bristol Bay.

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1.0 Introduction

Mineral exploration for copper, gold, and molybdenum has been ongoing at the Pebble deposit, near Iliamna, Alaska, since 1986 (Figure 1). Exploration intensified in 2002 with the transfer of mining claims from Cominco Alaska Exploration to Northern Dynasty Minerals, Inc. (NDM). The higher-grade Pebble East deposit was discovered in 2005. NDM joined with the global mining company Anglo-American in 2007 to form the Pebble Limited Partnership (PLP). With the increased activity after 2002 came increased public interest in the Pebble Project.[1]

The Pebble deposit lies within watersheds important to Bristol Bay salmonid populations and indigenous subsistence use of streams and fish.[2] The major surface waters near or within the Pebble Project include the South Fork Koktuli River, North Fork Koktuli River, Upper Talarik Creek, the Newhalen River, Iliamna Lake, the Kvichak River, and the Mulchatna River. Depending on the final locations of proposed mine facilities, additional waters could be placed at risk if the mine is developed, including Kaskanak Creek, the Stuyahok River, the Chulitna River, and Lower Talarik Creek.

The objectives of the 2009-2010 surface water sampling were to:

1. Collect surface water quality samples at locations already sampled by PLP for their environmental baseline program. Seven locations were co-located with PLP surface water quality sites. Sampling at these locations allowed comparison with PLP water quality results from sampling events between 2004 and 2007 under similar seasonal or hydrologic conditions.
2. Capture the potential range of natural variability of water quality during and after spring breakup. Surface water sampling events were conducted in May 2009, June 2009, and June 2010. The May event is important due to the significant increase in discharge caused by the ice breaking up and increased runoff due to snowmelt. Breakup periods are typically when metal concentrations are expected to be at their highest in the streams and then will decrease during more average flows during the summer (e.g., June sampling events).
3. Coordinate data collection in June 2010 for the collection of physical (physical habitat, discharge), chemical (surface water quality, sediment chemistry), and biological (macroinvertebrate, diatom, algae, fish) parameters. Field efforts were coordinated spatially and temporally so that interrelationships could be examined and the watershed ecology could be better understood.

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[1] See Chambers 2010 for discussion of the increase in mining activity after 2002

[2] Woody and O'Neal 2010; http://www.nature.org/ourinitiatives/regions/northamerica/unitedstates/alaska/howwework/Bristol-Bay-Headwaters-Field-Study.xml

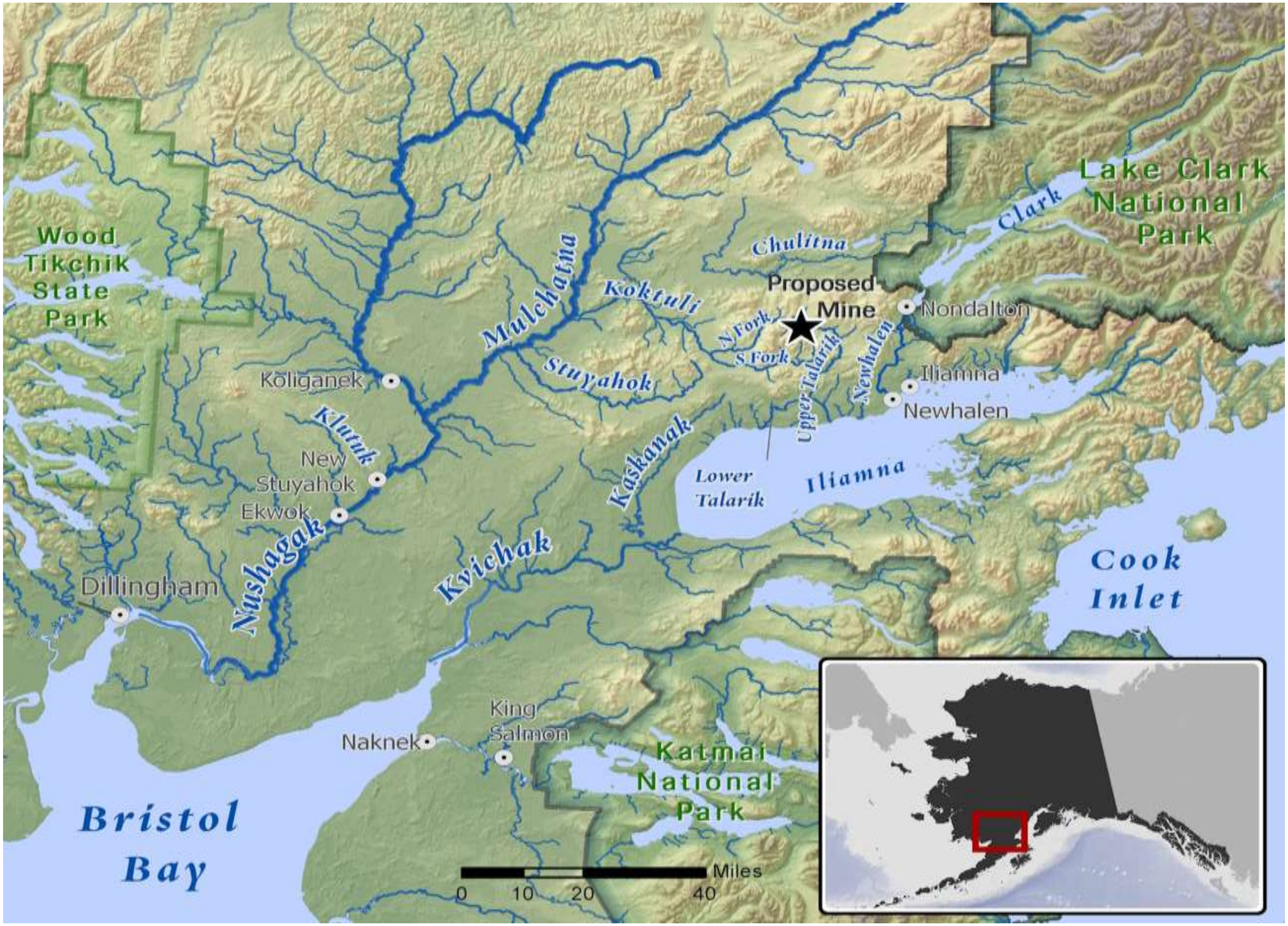

Figure 1. Location of the Pebble Deposit in the Bristol Bay Watershed, Southwest Alaska.

2.0 Study Area and Sampling Locations

The study area is within the Pebble Prospect, which is located 200 miles (320 km) southwest of Anchorage, Alaska. The site is north of Iliamna Lake, near the villages of Nondalton, Newhalen, and Iliamna, in a remote and usually uninhabited part of the Bristol Bay watershed (Figure 1). The Pebble Prospect sits on a drainage divide between Upper Talarik Creek and the Koktuli River, which form the headwaters of these two anadramous rivers draining into Bristol Bay.

Frying Pan Lake, located in a proposed tailings storage area at the Pebble site, drains into the South Fork Koktuli River, which then joins the North Fork Koktuli to form the Koktuli River that flows into the Mulchatna River, a tributary of the Nushagak River. The Nushagak River empties into Bristol Bay near the town of Dillingham. The Upper and Lower Talarik Creeks drain into Iliamna Lake which empties into Bristol Bay through the Kvichak River. Bristol Bay is the most valuable commercial salmon fishery in the United States and is one of the few remaining salmon strongholds in the world. The creeks are also known for excellent rainbow trout fishing, and Iliamna Lake is the largest freshwater lake used by sockeye salmon.

The region around the Pebble deposit is hydrologically and geologically complex. Thick, permeable glacial material allows for rapid exchange between surface water and groundwater,[3] resulting in groundwater with high oxygen content. It is the upwelling of this groundwater into streambeds that provides fish eggs with an oxygen-saturated environment throughout the winter. According to the PLP surface water quality data, the waters have low solute concentrations and low alkalinity (~10-30 mg/L $CaCO_3$), which may cause these waters to have a higher susceptibility to stream acidification and metal toxicity to fish. These surface waters also have low concentrations of copper and dissolved organic carbon (DOC), and low hardness values.

Seven of the PLP surface water sampling sites on the North Fork and South Fork Koktuli rivers and the Upper Talarik Creek and Kaskanak Creek were sampled for this study. Other rivers sampled include the Chulitna River and Newhalen River, and they are both important for subsistence users. The Chulitna River, a non-salmon bearing river, supports subsistence fish species such as northern pike and humpback whitefish, and flows north of the Pebble deposit, emptying into Lake Clark in the Lake Clark National Park and Preserve. The Newhalen River hosts salmon and connects Iliamna Lake with Six-Mile Lake and Lake Clark. Southwest of the Pebble deposit, the headwaters of Kaskanak Creek and the Stuyahok River are within mining claims areas and geographically close to the South Fork Koktuli near its confluence with the North Fork Koktuli. Kaskanak Creek runs south to join the Kvichak River. The Stuyahok runs west to the Mulchatna River. Kaskanak Creek, Stuyahok River, Rock Creek, and Groundhog Creek were sampled for The Nature Conservancy (TNC) study to expand our understanding of the water quality in the region beyond the Pebble deposit (Table 1, Figure 2, Appendix A). The tributaries on the Chulitna River, Rock Creek, and Groundhog Creek flow north into Lake Clark.

[3] Wobus 2009

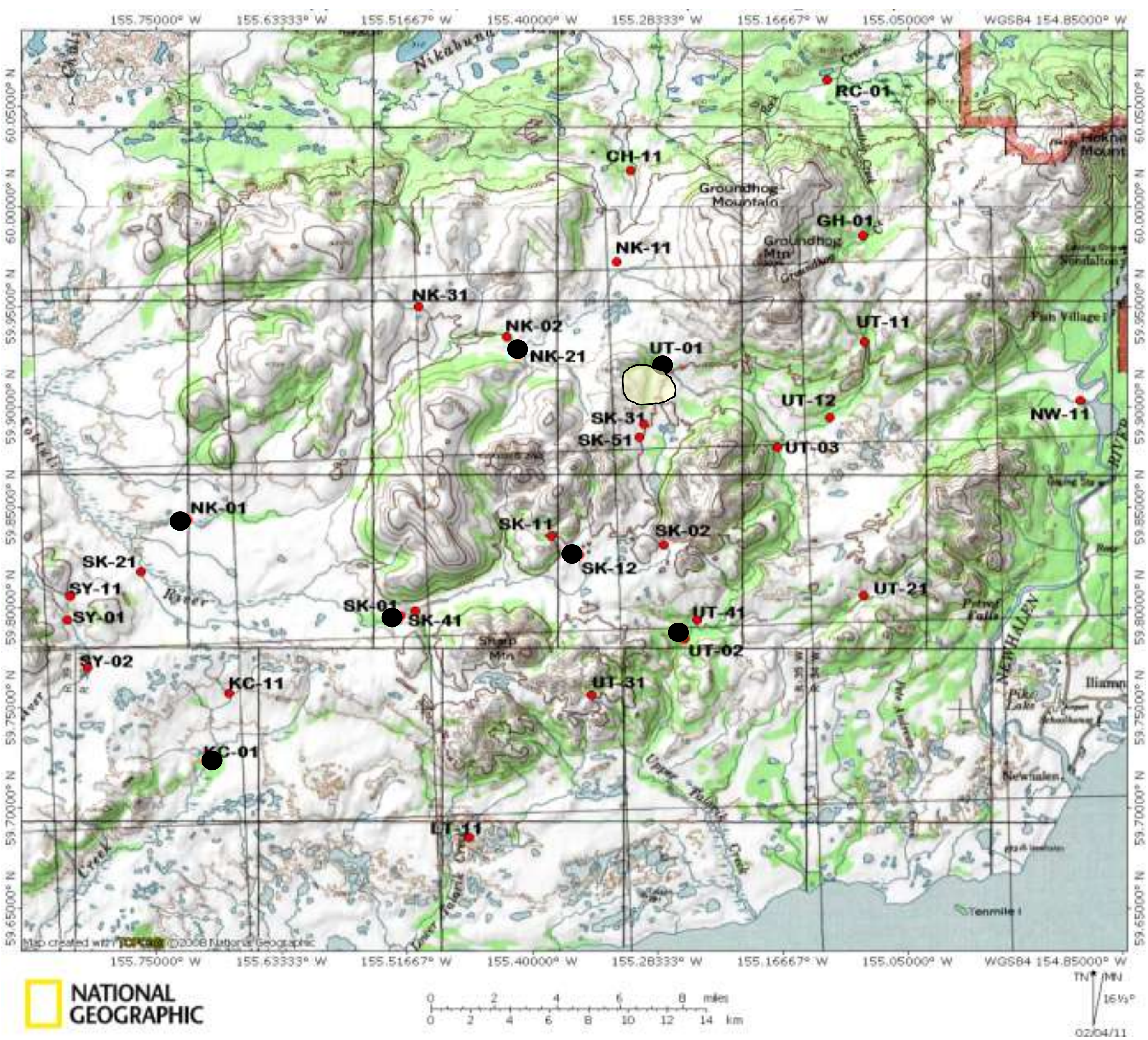

Figure 2. 2009-2010 Surface Water Sample Locations.

Legend

Pebble Deposit

TNC sites collocated with PLP sites

TNC unique sites

TNC – The Nature Conservancy

PLP – Pebble Limited Partnership

Table 1 Surface Water Sample Locations

Region	Site	Description	Rationale	5/09	6/09	6/10	PLP site	Coordinates
South Fork Koktuli	SK-01	main stem	USGS gage station; historical water quality data available; benthic sampling upstream 2008	x	x		SK100B	59.79668N, -155.51553W
	SK-02	main stem	copper bioavailability site; facilitate benthic sampling			x		59.83046N, -155.277181W
	SK-11	tributary	expand coverage of tributaries	x				59.83521N, -155.38141W
	SK-12	tributary	historical water quality data available; benthics sampled 2008		x	x	SK124A	59.82547N, -155.35619W
	SK-21	tributary	expand coverage of tributaries; possible hydrologic connection with Kaskanak; benthics sampled 2008	x	x			59.81877N, -155.76349W
	SK-31	tributary	expand coverage of headwaters on ore deposit		x	x		59.89077N, -155.29523W
	SK-41	tributary	benthics interannual site			x		59.79788N, -155.51015W
	SK-51	tributary	sampled by fish crew, near main camp			x		59.88454, -155.29927
North Fork Koktuli	NK-01	main stem	USGS gage; historic water quality data available; drilling expected nearby soon	x	x	x	NK100A1	59.984037N, -155.71301W
	NK-02	main stem	copper bioavailability study site			x		59.93433N, -155.42281
	NK-11	tributary	expand coverage of headwaters	x	x	x		59.9717N, -155.32068W
	NK-21	tributary	historic water quality data available	x	x		NK119B	59.92602N, -155.41106W
	NK-31	tributary	expand coverage of headwaters		x			59.94896N, -155.50639W
Upper Talarik Creek	UT-01	main stem	historic water quality data available; sampled for fish 2008	x	x	x	UT100E	59.9182N, -155.27770W
	UT-02	main stem	USGS gage; historic water quality data available; benthics sampled 2008; copper bioavailability study site	x	x	x	UT100B	59.7853N, - 155.25462W
	UT-03	main stem	immediately downstream of where a long tributary enters; PLP gage			x		59.87925N, -155.17116W
	UT-11	tributary	expand coverage of headwaters; good location for monitoring if mining proceeds	x	x	x		59.93103N, -155.08926W
	UT-12	tributary	wetland environment, possibly carbon rich, near pond system			x		59.82429N, -155.12238W
	UT-21	tributary	expand coverage of headwaters		x			59.80526N, -155.09073W
	UT-31	tributary	expand coverage of headwaters		x			59.75567N, -155.34494W
	UT-41	tributary	water for this tributary is expected to be groundwater coming from South Fork Koktuli			x		59.79326N, -155.24615W

Region	Site	Description	Rationale	5/09	6/09	6/10	PLP site	Coordinates
Lower Talarik Creek	LT-11	tributary	expand coverage of important streams	x	x			59.68488N, -155.45863W
Kaskanak Creek	KC-01	main stem	possible hydrologic connection with South Fork Koktuli; historic water quality data available; drilling announced nearby 10/2009	x	x	x	KC100A	59.72369N, -155.70262W
	KC-11	tributary	expand coverage of tributaries; drilling announced nearby 10/2009		x			59.75638N, -155.68242W
Stuyahok River	SY-01	main stem	expand coverage of important streams; drilling announced nearby 10/2009		x			59.79281N, -155.83214W
	SY-02	main stem	potentially more likely to receive water from South Fork Koktuli than SY-01 if there is a connection between drainages			x		59.76953N, -155.81289W
	SY-11	tributary	expand coverage of tributaries; possible hydrologic connection with South Fork Koktuli	x	x			59.79884N, -155.83151W
Lake Clark Region	CH-11	tributary to Chulitna River	expand coverage of streams to Lake Clark National Park; limited historic water quality data	x	x	x		60.017N, -155.30782W
	GH-01	tributary to Rock Creek	expand coverage of streams to Lake Clark National Park		x			59.98456N, -155.09117W
	RC-01	Rock Creek; tributary to Lake Clark	expand coverage of streams to Lake Clark National Park		x			60.01682N, -155.12488W
	NW-11	tributary to Newhalen River	expand coverage of locally important rivers; possible hydrologic connection with Upper Talarik; benthics sampled 2008	x	x	x		59.90273N, -154.88974W

3.0 Methods, Data Availability, and Relevant Standards

3.1 METHODS

Sampling was conducted in May 2009, June 2009, and June 2010. Surface water samples were collected for laboratory analysis from 14 sites in May 2009, 22 sites in June 2009, and 18 sites in June 2010. Seven sites were co-located with PLP surface water sites. Field measurements collected at each site included stream width, depth, and discharge, temperature, pH, conductivity, specific conductance, and dissolved oxygen.

Discharge was measured in cubic feet per second using a Marsh-McBirney current meter at 60 percent depth at 20-30 sections across each stream, or at six-inch intervals for very small streams. Depth was measured to the nearest 0.05 foot, and width was measured as wetted width.

Surface water samples were usually collected at mid-depth in mid-stream or at the thalwag. Stream water was drawn into pre-preserved sample bottles with a peristaltic pump through silicone or Teflon® tubing. Filtering for dissolved metals was conducted immediately on the stream bank. Samples were kept cool and transported within 48 hours to the Columbia Analytical Services, Inc. laboratory in Kelso, Washington. In May 2009, replicate samples were collected at each location; a single set of samples was collected and analyzed for gross alpha and beta radionuclides. Low-level mercury was only analyzed in May and June 2009 samples. All the surface water parameters are listed in Table 2.

Detailed field collection and laboratory analytical methods are available in the 2009 and 2010 Field Sampling Plans.[4] All 2009-2010 analytical and quality assurance/quality control (QA/QC) results are available from TNC.

3.2 AVAILABLE DATA

Cominco collected minimal surface water quality information from 1991 to 1993 in the exploration area;[5] Northern Dynasty and the PLP have collected information almost monthly since 2004. PLP released preliminary 2004 to 2007 surface water quality data in December 2008.[6]

3.3 WATER QUALITY STANDARDS

The State of Alaska recognizes water quality standards for fresh water based on the following uses: drinking water, irrigation, livestock watering, aquaculture, industrial, recreation, growth and propagation of aquatic life, and harvesting aquatic life for consumption. All waters are, by default, considered of adequate quality for all uses unless demonstrated otherwise.[7] In this document, the term "relevant standard" is used to refer to the most stringent water quality standard of any use as listed in the Alaska Department of Environmental Conservation (ADEC) 2008 *Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances*.[8] Where hardness or pH are relevant, they were measured in the laboratory and utilized in developing a relevant standard (Table 2). In Table 2,

[4] Zamzow 2009a; Zamzow 2010
[5] ADNR File 1033, date unknown, made available for a single day electronically
[6] PLP 2008 Pre-Permit Report F; Northern Dynasty Ltd. data from 2004 is presented in context in NDM 2005
[7] ADEC 2008; ADEC 2009
[8] ADEC 2008. The benchmark for sulfate is taken from ADEC 2009

the standard for total ammonia listed in the State of Alaska standard for fish-bearing waters is at pH 7 and temperature of 0-14 ^{o}C; the US EPA recommendation for un-ionized ammonia is also listed (0.02 mg/L).[9] The ADEC recommends alkalinity to be 20 mg/L "unless natural conditions are less". A hardness of 15 mg/L is used in calculating hardness-based standards, based on the median hardness of all TNC sample sites. All standards come from ADEC 2008, except sulfate and total dissolved solids are from ADEC 2009.

[9] US EPA 1976

Table 2 Surface Water Parameters for Laboratory Determination, Including Method Reporting Limits, Relevant Standards, and Use Category.

Analysis	Units	Method Reporting Limit	Relevant Standards	Use Category
Dissolved organic carbon	mg/L	0.5	none	
Nitrate + nitrite as N	mg/L	0.05	10	DW
Ammonia as N**	mg/L	0.01	5.9 as total ammonia; 0.02 as un-ionized	CCC
Alkalinity as $CaCO_3$	mg/L	2	20	CCC
Chloride	mg/L	0.2	230	DW
Fluoride	mg/L	0.2	1	IRR
Sulfate	mg/L	0.2	250	DW
Aluminum	µg/L	2	87	CCC
Iron	µg/L	20	1000	CCC
Calcium	µg/L	50	none	
Magnesium	µg/L	20	none	
Sodium	µg/L	100	none	
Potassium	µg/L	2,000	none	
Antimony	µg/L	0.05	6	DW
Arsenic	µg/L	0.5	10	DW
Cadmium*	µg/L	0.02	0.07	CCC
Chromium	µg/L	0.2	100	DW
Copper*	µg/L	0.1	1.84 T, 1.77D	CCC
Lead*	µg/L	0.02	0.28T, 0.3D	CCC
Manganese	µg/L	0.05	50	HC
Molybdenum	µg/L	0.05	10	IRR
Nickel*	µg/L	0.2	10.5	CCC
Selenium	µg/L	1	5	CCC
Uranium	µg/L	0.02	30	DW
Zinc*	µg/L	0.5	24.0T, 23.7D	CCC
Mercury*	µg/L	1	0.05	HC
TDS	mg/L	5	500	DW
TSS	mg/L	5	none	
Cyanide (total)	mg/L	0.01	5.2	CCC
Gross alpha (radionuclides)	pCi/L	2	15	DW
Gross beta (radionuclides)	millirem	***	4	DW

Notes:

Method reporting limit is provided by Columbia Analytical Services Inc. laboratory. * hardness dependent **pH dependent *** gross beta is measured as picoCuries per liter (pCi/L) in the lab, but is regulated as millirems (US EPA 2002). µg/L = micrograms per liter; DW = drinking water; CCC = freshwater aquatic life, chronic criteria; D=dissolved fraction for metals; IRR = irrigation; HC = human consumption of aquatic organisms; mg/L = milligrams per liter; T = total; TDS = total dissolved solids; TSS =t otal suspended solids.

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4.0 Results

Nearly all the parameters, including total and dissolved metals, alkalinity, DOC, conductivity, and major anions and cations, were found at low concentrations. Some parameters (e.g., cyanide, fluoride, and selenium) were non-detect at almost every sampling location. Mercury was only detected in samples subjected to low-level mercury analysis.

Most of the parameter concentrations met relevant standards, even the total metal concentrations from samples collected during breakup in May 2009 when metals can be elevated. Aluminum, a common erosional material, was measured above relevant standards 15 times; lead, six times; copper, five times; manganese, three times; and iron and cadmium exceeded the relevant standard twice over the two-year sampling period. In June 2010, other than low alkalinity, no constituents were greater than relevant standards, except for cadmium (once), copper (two tributaries near the Pebble deposit), and aluminum (Stuyahok and Kaskanak sites, and one tributary near the Pebble deposit). Details are provided in Sections 4.4 and 4.5.

4.1 Quality Assurance/Quality Control Results

For the 2009 and 2010 samples, field replicates were collected extensively as a QA/QC data objective. An evaluation of the QA/QC results confirms that the data collected for this study is of high quality with good agreement between replicates and no introduced contamination (TNC, unpubl. report).

Sample collection methods were designed to minimize contamination at the remote sampling sites. To maintain the cleanest possible sampling equipment, sampling was conducted using clean-hands technique and through application of a peristaltic pump and tubing (with in-line filter for dissolved fractions) to pump stream water directly into pre-preserved sample bottles; tubing and filters were replaced at every site.

Baseline surface water was expected to have low concentrations of most parameters, and be easily impacted by contaminants. Quality controls in both the laboratory and the field were used to assess whether concentrations in field samples represented the "true" condition of the surface water. The overall conclusion is that most parameters are present in low concentrations, and field sample measurements represent a "true" condition of the natural stream water, with the exception that laboratory analysis may cause zinc to vary by about 1 µg/L, and variability of up to 6 µg/L was observed in field replicates.

4.2 Field Parameters

The measured field parameters included conductivity, specific conductance, pH, dissolved oxygen, and water temperature (Table 3, Appendix A). The field parameter results confirm that the region can be generally characterized as having cold, well-oxygenated waters with low conductivity and neutral pH. The pH was consistent across all sites, with the exception of a Stuyahok River tributary with very low pH. Conductivity values were similar across sites, but median values were slightly higher in the Upper and Lower Talarik Creeks. In May, the pH was slightly more acidic[10] and conductivity and temperature values were lower. The impacts on parameters due to the breakup event sampled in May 2009 are discussed in Section 5.1.1.

[10] These pH assessments are based on lab pH due to possible inaccurate readings of field pH in May 2009.

Table 3 Summary of 2009-2010 Field Parameter Results

		Temp (^oC)	DO (mg/L)	Field pH	Lab pH	Field Conductivity (µS/cm)	Field Specific Conductance (µS/cm)	Lab Specific Conductance (µS/cm)
North of Pebble Prospect	Min.	2.2	9	6.3	7.1	14	22	32
	Max.	9.6	13	7.6	7.6	43	68	64
	Median	6.1	11	7.1	7.2	31	48	56
North Fork Koktuli	Min.	0.0	11	5.3	6.2	8	15	23
	Max.	8.9	13	7.6	7.7	48	68	65
	Median	7.4	11	7.0	7.1	23	35	39
South Fork Koktuli	Min.	0.2	10	5.4	6.3	6	11	21
	Max.	15.5	14	7.5	7.6	58	84	78
	Median	6.4	11	6.9	7.1	27	37	42
Upper and Lower Talarik	Min.	0.1	9	5.9	6.6	13	22	34
	Max.	15.5	15	8.5	7.6	158	98	97
	Median	5.8	12	7.3	7.4	30	45	52
Southwest of Pebble Prospect	Min.	0.1	8	2.8	5.4	3	5	9
	Max.	12.4	14	7.5	7.2	31	46	45
	Median	7.8	11	6.9	6.8	17	25	32
All Sites	Min.	0.0	8	2.8	5.4	3	5	9
	Max.	15.5	15	8.5	7.7	158	98	97
	Median	6.5	11	7.1	7.2	26	38	45

Notes:

Temp = water temperature; DO = dissolved oxygen; ^oC = degrees Celsius**;** µS/cm = microSiemens per centimeter; mg/L = milligrams per liter; Min. = minimum; Max. = maximum

North of Pebble Prospect includes streams on Groundhog Mountain and tributaries to the Newhalen and Chulitna rivers. Southwest of the Pebble Prospect includes the Kaskanak Creek and the Stuyahok River sampling locations.

Stream width, depth, and discharge were measured at sample sites (Table 4). Due to dangerously high flow conditions, discharge was not measured at NK-01 or UT-02 in May and June 2009, or at SK-01 in June 2009. All three of these sites were located at USGS gages and discharge or flow information from USGS is provided. In May 2009, all U.S. Geological Survey (USGS) gages were non-operational due to ice or equipment failure and flow during this period is estimated. The May 2009 sampling event was scheduled to occur during the rising limb of the hydrograph on Upper Talarik Creek and just prior to the rising limb on the main stems of North and South Fork Koktuli Rivers.

Based on estimated USGS gage information (Appendix B), flows increased on the main stem of the rivers into mid-May 2009 and then decreased by the time June 2009 samples were collected. Flow measurements in June 2010 indicated that there was less snowmelt than in 2009.

Table 4 2009-2010 Stream Discharge Information

			Stream Discharge	
Watershed	Site ID	Date	width (ft)	discharge (cfs)
North of Pebble Prospect	NW-11	5/1/2009	33.0	155
		6/8/2009	38.2	85
		6/9/2010	38.5	44
	CH-11	5/3/2009	14.5	68
		6/5/2009	12.5	30
		6/7/2010	12.5	8
	RC-01	6/8/2009	14	41
	GH-01	6/3/2009	20	86
North Fork Koktuli	NK-01	5/2/2009	nd	*52[eA]
		6/6/2009	nd	*622[A]
		6/10/2010	76	29
	NK-02	6/7/2010	39	90
	NK-11	5/3/2009	9.4	6
		6/4/2009	5.3	6
		6/7/2010	12	1
	NK-21	5/3/2009	24.2	324
		5/4/2009	nd	nd
		6/6/2009	nd	nd
	NK-31	6/6/2009	11.5	13
South Fork Koktuli	SK-01	5/1/2009	67.0	136[†]
		6/6/2009	nd	*730[A]
	SK-02	6/8/2010	15.5	44
	SK-11	5/4/2009	11	20
	SK-12	6/6/2009	23	74
		6/9/2010	19	23
	SK-21	5/2/2009	47	279
		6/6/2009	20	77
	SK-31	6/5/2009	4	8
		6/10/2010	4	3
	SK-41	6/9/2010	28.5	27
	SK-51	6/7/2010	6.5	2

			Stream Discharge	
Watershed	Site ID	Date	width (ft)	discharge (cfs)
Upper Talarik	UT-01	5/3/2009	13	40
		6/5/2009	10	23
		6/10/2010	14	10
	UT-02	5/2/2009	nd	*110[eA]
		6/5/2009	nd	*640[A]
		6/8/2010	57	198
	UT-03	6/10/2010	33	109
	UT-11	5/1/2009	14.0	83
		6/5/2009	19.5	57
		6/10/2009	13	19
	UT-12	6/8/2010	18	33
	UT-21	6/8/2009	15	30
	UT-31	6/8/2009	6.5	6
	UT-41	6/9/2010	7.3	3
Lower Talarik	LT-11	5/2/2009	60	131
		6/7/2009	30.3	71
Kaskanak Creek	KC-01	5/2/2009	nd	nd
		6/7/2009	26	49
		6/9/2010	23	24
	KC-11	6/7/2009	7	6
Stuyahok River	SY-01	6/7/2009	9.5	13
	SY-02	6/9/2010	14	11
	SY-11	5/2/2009	9.9	81
		6/7/2009	3.5	2

Notes:

Flow was not measured in 2009 at sites NK-01 or UT-02 due to dangerous conditions or at SK-01 in June 2009.

† USGS information lists 40 cfs as the estimated flow; *USGS gage information, available at http://waterdata.usgs.gov/nwis

E = estimated ft = feet

A = approved cfs = cubic feet per second

Nfd = non-detect

4.3 MAJOR ELEMENTS

The major elements include major cations (e.g., calcium, sodium, magnesium, potassium) and major anions (e.g., bicarbonate, sulfate, fluoride, chloride). Fluoride concentrations were below the method reporting limit at all sites, and chloride, magnesium, and potassium concentrations were very low (Table 5). Most streams are bicarbonate-calcium type waters. At some sampling locations, there were significant differences in alkalinity and calcium concentrations between the May 2009 event and the June sampling events (Appendix C); this is discussed further in Section 5.1.1. The highest sulfate concentrations were measured in the South Fork Koktuli tributaries (e.g., SK-31, SK-11, and SK-12).

Hardness was calculated based on calcium and magnesium by K. Zamzow in 2009 and by the analytical laboratory in 2010. Bicarbonate was calculated by the laboratory in 2010 and was identical to alkalinity; bicarbonate for 2009 was presumed to be the value of alkalinity, given the neutral pH of the water.

Table 5 Summary of 2009-2010 Major Element Concentrations

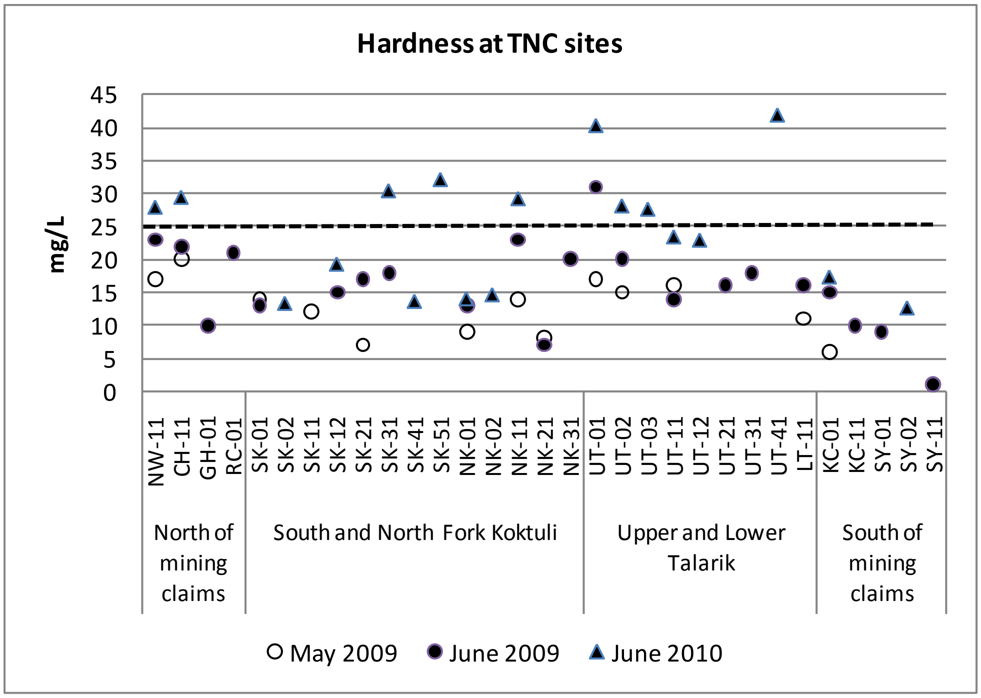
Region	Sampling Date	Ca (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Hardness (mg/L)
North of Pebble Prospect	May 2009	5	2	1-2	0.5-0.8	21-22	1-2	1	17-20
	June 2009	3-8	1-2	1-2	0.3-0.4	4-25	1-5	1	10-23
	June 2010	8-9	2-3	1-2	0.2-0.5	32-34	2-4	1	28-30
South Fork Koktuli	May 2009	2-4	1-2	1	0.3-0.4	9-16	2-4	1	7-14
	June 2009	4-5	1-2	1	0.2-0.5	11-20	3-10	1	13-18
	June 2010	4-9	1-4	1-2	0.2-0.7	14-42	4-20	1	13-32
North Fork Koktuli	May 2009	2-4	1-2	1	0.3-0.9	9-12	1-2	1	8-14
	June 2009	2-6	1-3	1-2	0.1-0.7	11-28	1-2	1	7-23
	June 2010	4	2	1-2	0.2-0.5	18-40	2	1	14-29
Upper and Lower Talarik	May 2009	3-5	2	1-2	0.3-0.6	14-20	2-3	1	11-17
	June 2009	4-8	1-3	1-3	0.2-0.5	20-31	2-5	1	14-31
	June 2010	7-14	2-4	1-3	0.2-0.5	26-49	3-8	1	23-43
Southwest of Pebble Prospect	May 2009	0-2	1	0-1	0.4-0.6	0.5-5	1	1	1-6
	June 2009	0-4	1-2	0-1	0.1-0.4	4-22	1-4	1	1-15
	June 2010	4-5	2	1	0.2-0.4	15-25	2-3	1	13-17
Range		0-14	1-4	1-3	0.1-0.9	0.5-49	1-20	1	1-43
Median of monthly means		4.9	1.9	1	0.3	21	2	1	15

Notes: Ca= calcium; Na=sodium; Mg=magnesium; K=potassium; HCO_3=bicarbonate; SO_4=sulfate; Cl-chloride; mg/L = milligrams per liter

Differences in alkalinity can be observed between sampling events and spatially within a watershed. Spatially, the lowest alkalinity is observed southwest of the Pebble Prospect at an ephemeral tributary (SY-11), and on Kaskanak Creek (KC-01) in May 2009, with alkalinities below 6 mg/L. The Upper Talarik generally had the highest alkalinity. Typically waters sampled in May 2009 during breakup had lower alkalinity than waters sampled in June. There was also a variation between years, with sites in June 2010 generally having higher alkalinity than the same sites sampled in June 2009. Discharge information indicates that there was less snowmelt in 2010, and this may explain the difference in the alkalinity values.

Hardness was lowest during breakup in May and highest in June 2010 (Figure 3). In 2009, only one site had hardness values above the ADEC recommended value of 25 mg/L.

Figure 3. 2009-2010 Hardness Values at TNC Sampling Locations.



Notes: TNC = The Nature Conservancy North of mining claims and South of mining claims refers to sampling locations north and southwest of the Pebble Prospect, respectively.

4.4 Minor Elements

The minor elements analyzed by the analytical laboratory included aluminum, iron, manganese, nitrogen (nitrate + nitrite, ammonia) and DOC (Appendix D).

Aluminum, iron, and manganese are typically derived from erosion of soils, rock outcrops, and glacial-alluvial materials. Total or particulate iron and manganese were rarely measured above relevant standards and particulate aluminum exceeded relevant standards at 9 of 14 sites in May 2009, but only at 3 of 22 sites in June 2009 and in 2 of 18 sites in June 2010 (Table 6). Particulate concentrations typically increased during breakup, and the highest concentrations of aluminum, iron, and manganese occurred in May 2009. Iron was elevated above ADEC standards at two sites in May 2009.

Ammonia and nitrate + nitrite were present in very low concentrations and all were below the relevant standards. The DOC concentrations were also low, with only four samples greater than 4 mg/L and 6 mg/L was the highest DOC concentration. The highest DOC concentrations typically occurred in May 2009.

Table 6 Summary of 2009-2010 Aluminum, Iron, and Manganese Concentrations

Watershed	Month	n	Aluminum (µg/L) Total	Aluminum (µg/L) Dissolved	Iron (µg/L) Total	Iron (µg/L) Dissolved	Manganese (µg/L) Total	Manganese (µg/L) Dissolved
	Relevant Standards		***87 µg/L***		***1,000 µg/L***		***50 µg/L***	
North of Pebble Prospect	May 2009	2	299-**1027**	18-32	691-**1510**	137-222	33-**103**	20-**67**
	June 2009	4	42-70	10-21	187-334	76-158	9-33	3-26
	June 2010	2	38-**147**	9-11	189-530	83	13-**61**	11-51
South Fork Koktuli, Upper	May 2009	1	452	44	702	71	51	31
	June 2009	2	81-**197**	19-25	377-518	32-161	31-35	13-25
	June 2010	4	31-52	7-12	147-411	28-213	13-48	8-45
South Fork Koktuli, Lower	May 2009	2	34-61	9-31	66-88	18-28	8-12	7-12
	June 2009	2	9-43	3-25	16-137	6-31	1-7	1-4
	June 2010	1	18	5	45	<20	3	1
North Fork Koktuli	May 2009	3	36-**140**	13-41	175-253	76-125	11-44	7-40
	June 2009	4	37-79	8-25	102-596	51-317	9-24	3-13
	June 2010	3	9-31	3-13	56-241	90-94	9-14	6-10
Upper and Lower Talarik	May 2009	4	35-**330**	12-28	126-646	56-122	20-37	8-35
	June 2009	6	33-74	8-14	88-217	26-65	4-11	2-6
	June 2010	6	17-63	4-10	46-288	<20 - 120	4-24	1-20
Southwest of Pebble Prospect	May 2009	2	141-**972**	55-77	44-**1070**	16-199	29-38	28-31
	June 2009	4	38-**218**	22-**119**	26-515	26-222	3-17	2-15
	June 2010	2	51-**136**	16	438-601	221-256	15-18	13-17

Note: Bolded values exceed the relevant standard.

µg/L = micrograms per liter

4.5 TRACE ELEMENTS

The trace elements measured in the surface water samples included radionuclides (gross alpha and gross beta), antimony, arsenic, chromium, cyanide, mercury, molybdenum, nickel, selenium, and uranium, all found in very low concentrations (Table 7).

Table 7 Summary of 2009-2010 Trace Elements Results

Parameter	Relevant Standard	Units	Minimum	Maximum
gross alpha	15	pCi/L	< 1.5	1.8
gross beta	*	pCi/L	<1.5	3.3
Antimony	6	µg/L	<0.01	0.09
Arsenic	10	µg/L	< 0.10	3.9
Chromium	100	µg/L	0.09	1.09
Cyanide	5.2	µg/L	< 0.01	< 0.01
Mercury	50	ng/L	0.4	5.4
Molybdenum	10	µg/L	<0.02	3.2
Nickel	10.5	µg/L	0.05	0.94
Selenium	5	µg/L	<0.3	0.3
Uranium	30	µg/L	<0.003	0.12

Notes:

*The relevant standard for gross beta is 4 millirems but is measured in the laboratory in picoCuries per liter (pCi/L); a conversion is required to determine millirems. The conversion was not calculated, but all samples were less than the laboratory lower limit of detection.
µg/L = micrograms per liter; ng/L = nanograms per liter

Other trace elements that were analyzed include cadmium, copper, lead, and zinc and were found at detectable levels (Table 8, Appendix D). Relevant standards for cadmium, copper, lead, and zinc are hardness dependent. A hardness of 15 mg/L was used when calculating the relevant standards, which was the median of hardness at sites sampled in 2009-2010. Where replicates were collected, the mean of replicates was utilized in assessing the median concentration.

The South Fork Koktuli tributary that drains Kaskanak Mountain (SK-11/12) had cadmium, copper, and lead concentrations above relevant standards (Figure 4). The sampling location (SK-31) near the Pebble deposit also had copper concentrations above relevant standards (Figure 4 and Figure 5). The total lead concentrations at a Chulitna tributary (CH-11) and Kaskanak Creek (KC-01) were above relevant standards, and concentrations were slightly above at Newhalen River (NW-11) and Upper Talarik Creek (UT-02) in May 2009 (Figure 4).

Dissolved lead, dissolved cadmium, and total and dissolved zinc were not measured above relevant standards. Further discussion of elevated metal concentrations is found in Section 5.1.2.

Table 8 Summary of 2009-2010 Cadmium, Copper, Lead, and Zinc Concentrations

Parameter	Dates	Relevant Standard (µg/L)	Minimum	Maximum	Median of Replicate Means	Sites with Concentrations Exceeding Relevant Standards (concentration in parentheses)
Cadmium, total	all	0.07	<0.005	0.091	0.01	SK-11, May 2009 (0.08), SK-12, June 2009 (0.09)
Cadmium, dissolved	all	0.07	<0.005	0.046	0.007	none
Copper, total	May 2009	1.8	0.11	2.56	0.29	SK-11 (2.56)
	June 2009		0.04	5.6	0.21	SK-12 (5.6), SK-31 (5.3)
	June 2010		0.1	4.40	0.20	SK-12 (2.3), SK-31 (4.4)
Copper, dissolved	May 2009	1.77	0.07	0.58	0.19	none
	June 2009		0.05	3.57	0.15	SK-12 (1.89), SK-31 (3.57)
	June 2010		0.10	2.50	0.20	SK-31 (2.5)
Lead, total	May 2009	0.28	0.03	0.6	0.16	CH-11 (0.6) SK-11 (0.54), KC-01 (0.43), NW-11 (0.34), UT-02 (0.29)
	June 2009, June 2010		0.01	0.9	0.03	SK-12 June 2009 (0.9)
Lead, dissolved	all	0.3	0.01	0.08	0.01	none
Zinc, total	all	24	0.3	15.3	1.5	none
Zinc, dissolved	all	24	0.2	10.5	1.6	none

Notes: µg/L = micrograms per liter

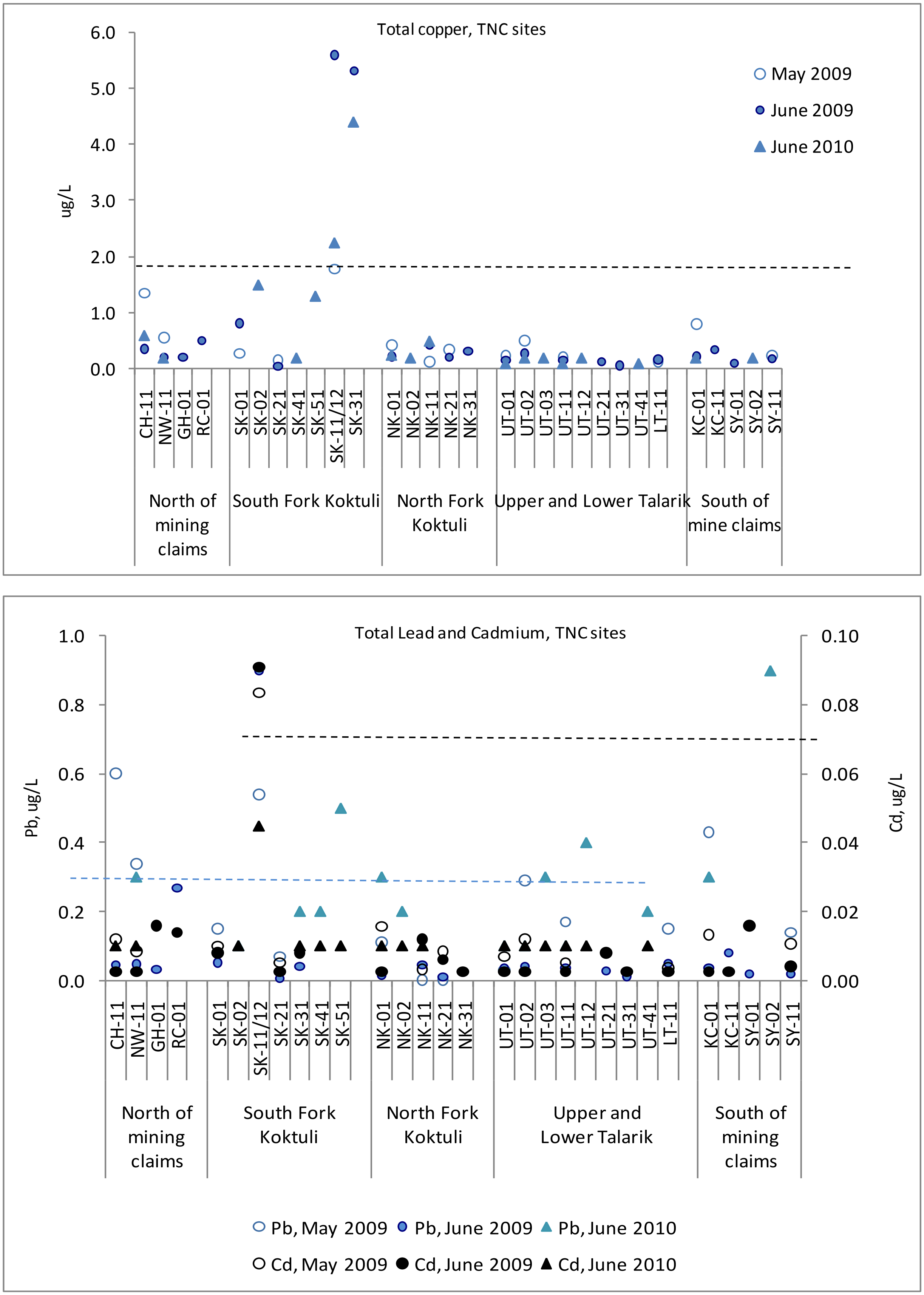


Figure 4. Total Copper, Cadmium, and Lead Results.

Dotted lines represent the relevant standards based on 15 mg/L hardness value: 1.8 µg/L (copper), 0.3 µg/L (lead), 0.07 µg/L (cadmium). mg/L= milligrams per liter; µg/L= micrograms per liter; TNC = The Nature Conservancy.

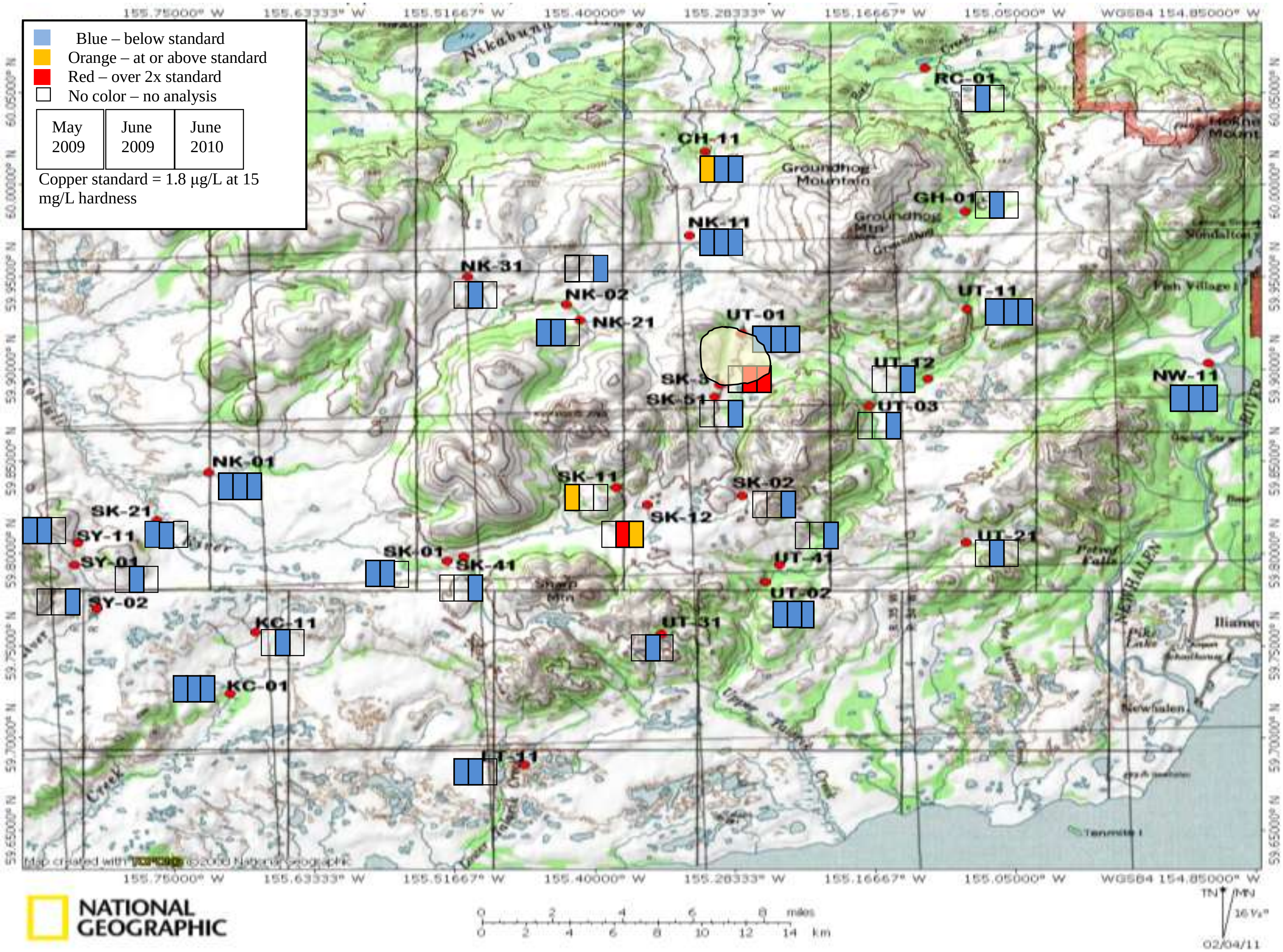


Figure 5. Total Copper Concentrations at 2009-2010 Sample Locations.

Tan area represents the Pebble deposit.

5.0 Discussion

The objectives of the study were to sample during and after breakup in 2009 and in June 2010 to better understand local water chemistry as it relates to potential risk to wild salmon from large-scale mining in the region. Sample locations were selected at sites that have been monitored by PLP as well as additional locations outside the PLP monitoring area to expand the coverage to neighboring watersheds. The June 2010 event was also part of a co-located abiotic and biotic sampling program. Water quality results are discussed in Section 5.1, with the impact of breakup discussed in Section 5.1.1, elevated metal concentrations are discussed in Section 5.1.2 and a comparison with the PLP data is provided in Section 5.2. A discussion on groundwater-surface water interactions sites is provided in Section 5.3.

The chemical composition of the surface water in the study area is influenced by surface and bedrock geology, an increase in suspended solids due to increase in the discharge rates (e.g., during spring breakup), and groundwater contributions. Together, these affect the concentration, bioavailability, and toxicity of metals. Bedrock and surficial geology are the source of cations (e.g., calcium, magnesium, sodium, potassium) and anions (e.g., bicarbonate, sulfate) that define the alkalinity and hardness of the surface water and influence pH. Surface runoff contributes erosional particulates (e.g., aluminum, iron, manganese, lead), organic acids from soil, and organic carbon from decomposing material into the stream chemistry. Groundwater contributes major ions to seeps and in stream upwellings that influence the surface water chemistry. A summary of the regional characterization of the water quality is provided below.

5.1 REGIONAL WATER QUALITY CHARACTERIZATION

In the study area:

- Metal concentrations were generally below relevant standards, and generally higher during breakup as particulates. Dissolved metal concentrations were similar across the study area, except for higher concentrations at a site near the Pebble deposit (SK-31) and in a mineralized tributary (SK-11/12) that feeds into the upper reaches of the South Fork Koktuli River, which also had higher concentrations of minor and trace elements.
- Aluminum and iron were more consistently elevated southwest of the Pebble Prospect than in other regions, and manganese was higher in the Chulitna watershed. Total iron tended to be lowest along the Koktuli rivers and the Talarik creeks. The lower reaches of the South Fork Koktuli River had the lowest concentrations of aluminum, iron, and manganese.
- Conductivity (< 50 μS/cm) and specific conductance (<70 μS/cm) were low in all sites.
- pH was circum-neutral (6.2 – 7.7) at all but one site, and generally 0.5-1 units higher in June than in May.
- Alkalinity was low (less than 20 mg/L in May) in most regions and lowest in the southwest sampling locations. The Upper Talarik generally had higher alkalinity than the North and South Forks of the Koktuli.
- Hardness was less than 25 mg/L at all but one site and hardness values were higher at sites north of the Pebble Prospect and near the Pebble deposit.
- DOC concentrations were low (<6 mg/L) in all sampling locations.

- Sulfate and copper concentrations changed spatially along the length of the South Fork Koktuli. The upper reaches (SK-31, SK-51, SK-11/12, SK-02) typically had higher sulfate and copper concentrations relative to their location to the Pebble deposit, while the lower reaches (SK-21, SK-41, SK-01) had lower concentrations. Sulfate concentrations were also elevated at the Upper Talarik headwaters that lie near the Pebble deposit, but copper was not elevated at this site.

5.1.1 Importance of Breakup on Particulate Concentrations

Changes were observed in alkalinity and metals concentrations between the breakup sampling event in May 2009 and the June sampling events. Surface waters had lower alkalinity and hardness values and higher metal concentrations in May 2009 than in June when flows were significantly reduced.

During breakup, particulate material flushes out with snowmelt carrying metals on suspended sediment, and dust entrained in melting snow and ice may also contribute to the total metal load. Most sites sampled in May 2009 had particulate aluminum, iron, manganese, or lead measured above the most stringent water quality standards, but by June, the only sites with these metals above relevant standards were on the upper South Fork Koktuli River (SK-31, SK-51, SK-12) and outside the Pebble Prospect (SY-02, SY-11, KC-01, CH-11). Copper was only elevated at SK-31 and SK-12 in June.

In May 2009, when metals concentrations were higher due to breakup conditions, factors that affect metal toxicity are generally in low concentrations such as hardness (i.e., calcium and magnesium), alkalinity (i.e., bicarbonate), and pH.

The DOC concentration was 1-2 mg/L higher in May than in June, but generally below 4 mg/L at most sites. The DOC will only affect metals in the dissolved form, while most elevated metals detected in May 2009 were in the particulate form.

5.1.2 Elevated Metal Concentrations

Many of the sites sampled in May 2009 had erosional material, such as particulate aluminum, iron, manganese, or lead, above the most stringent water quality standards. Of 12 sites sampled in both May and June 2009, five sites (NK-11, NK-21, SK-01, SK-21, LT-11) had no metals above relevant standards in either month. Of the five sites, only NK-11 was also sampled in June 2010 and low levels of metals were again detected. Of the 21sites sampled in June 2009, only SK-12 had more than a single metal above relevant standards (aluminum, lead, and copper), and in June 2010 only CH-11 had more than a single metal above relevant standards, emphasizing the extraordinarily low metal content of the natural waters in the region after breakup, even in surface water very near the Pebble deposit.

Aluminum, Iron, Manganese, and Lead

The sampling locations with at least two of these metals (aluminum, iron, manganese, and lead) above relevant standards in May 2009 were sites (CH-11, KC-01, UT-02, NW-11, and SK-12) with the highest suspended sediment concentrations (16-52 mg/L). Two other sites had a single metal above standards in June 2009: KC-11 (aluminum) and SY-11 (aluminum). In June 2010, only CH-11 had more than a single elevated metal (aluminum, manganese), and site SY-02 had elevated aluminum concentrations. Both of these locations lie outside the Pebble Prospect.

Copper

Two sites on the upper South Fork Koktuli (SK-31 and SK-11/12) had copper concentrations above water quality standards for aquatic life, based on 15 mg/L hardness. The percent of total copper that was in the dissolved form was higher in the June sampling events than in May 2009, which suggests that metal concentrations in May were driven by erosional factors caused by spring breakup.

Site SK-31 had total and dissolved copper of 5.3 μg/L and 3.6 μg/L, respectively, in June 2009 and 4.4 μg/L and 2.5 μg/L, respectively, in June 2010 (the site was not sampled in May 2009). The SK-31 site is located on a small tributary in a wetland near the Pebble deposit. It also had higher sulfate concentrations relative to other sites in the area (10-20 mg/L) and with variable alkalinity (16 mg/L in June 2009; 42 mg/L in June 2010). At SK-31, the pH was neutral (7.1-7.3), calcium moderate (5-8 mg/L), and had low conductivity (30-77 μS/cm).[11] The mineralized rocks associated with the Pebble deposit are the likely source of sulfate and copper, but there appears to be enough neutralization capacity to maintain a neutral pH.

The second site (SK-11/12) is located along a narrow, shallow reach with a cobble streambed at the foot of Kaskanak Mountain. It fed another tributary that in turn flowed into the South Fork Koktuli below Frying Pan Lake. Particulate metal concentrations were elevated in May 2009 (manganese, aluminum, cadmium, copper, lead) and in June (aluminum, cadmium, copper, lead). In May 2009, total copper was greater than relevant standards (2.6 μg/L)[12] but dissolved copper was lower (0.6 μg/L). In June 2009, the site location was moved downstream and became SK-12; the total and dissolved copper concentrations were greater at the downstream site (5.6 μg/L and 1.9 μg/L, respectively, in June 2009, 2.3 μg/L and 1.5 μg/L, respectively, in June 2010). Although the site had some of the highest sulfate measured (6-10 mg/L),[13] the relatively neutral pH (6.2-7.1), total suspended solids (9-16 mg/L), and total copper indicated particulate material (dissolved copper was 23%, 34%, and 66% of total in May 2009, June 2009, and June 2010, respectively). The sites had low alkalinity (11-20 mg/L), moderate calcium (4-6 mg/L), and low conductivity (17-40 μS/cm).

5.1.3 Water Chemistry that Moderates Metal Toxicity

Generally elevated metals in May 2009 coincided with lower values in factors that can moderate metal toxicity, such as alkalinity, hardness, and pH (Table 9). Dissolved organic concentrations, which also can moderate metal toxicity, tended to be slightly higher in May than in the June sampling events.

Many of the sites sampled have alkalinity below the 20 mg/L concentration recommended by ADEC and therefore have little buffering capability (Figure 6). The pH at all the sites is near neutral except for the mountain tributary SY-11 (Stuyahok River). The Upper and Lower Talarik Creek sites generally have higher pH than the South and North Fork Koktuli River sites.

[11] Although the conductivity is low, it is relatively high for the region.
[12] Hardness-based water quality standards were calculated at 15 mg/L hardness, based on the low measured hardness of the waters. Actual hardness at this site was 12 mg/L in May 2009 and 15 mg/L in June 2009. At 15 mg/L, the relevant standard would be 2.6 μg/L.
[13] In 2009, only SK-31 had higher sulfate. In 2010, SK-31 and SK-51 (both close to the Pebble deposit) had higher sulfate concentrations.

Table 9 Parameters Affecting Metal Toxicity: Hardness, Alkalinity, pH and DOC

Region	Sample Date	Hardness (mg/L)	Alkalinity (mg/L)	Lab pH	DOC (mg/L)
North of Pebble Prospect	May 2009	**17-20**	21-22	7.2	3-4
	June 2009	**10-23**	**4**-25	7.1-7.6	2-4
	June 2010	28-30	25-34	7.2-7.3	2-4
South Fork Koktuli	May 2009	**7-14**	**9-16**	6.3-7.0	1-3
	June 2009	**13-18**	**11**-20	7.1-7.6	1-3
	June 2010	**13**-32	**14**-42	6.9-7.2	1-3
North Fork Koktuli	May 2009	**8-14**	**9-12**	6.2-6.9	4-6
	June 2009	**7-23**	**11**-28	7.3-7.7	2-4
	June 2010	**14**-29	**18**-40	7.1	1-2
Upper and Lower Talarik	May 2009	**11-17**	**14**-20	6.6-7.2	2-4
	June 2009	**14**-31	20-31	7.3-7.6	1-2
	June 2010	**23**-43	26-47	7.2-7.6	1-2
Southwest of Pebble Prospect	May 2009	**1-6**	**0.5-5**	**5.4**-6.5	5
	June 2009	**1-15**	**4**-22	**5.5**-7.2	1-3
	June 2010	**13-17**	**15**-25	6.7-6.9	3

Notes: Hardness is recommended to be 25 mg/L or greater; alkalinity 20 mg/L or greater; and pH 6-8 for aquatic life. Data points outside recommended concentrations are noted in bold font. mg/L= milligrams per liter.

Surface waters with low alkalinity have difficulty buffering acid, which means the pH will change easily when small amounts of acid are introduced. Groundwater passing rocks containing sulfide minerals may contribute mineral acid to seeps and surface waters, while surface runoff causes organic acids (e.g., humic, fulvic) to flush off soil and may also contribute mineral acidity if surface rock or the soil contains sulfides. Both processes probably occur in the Pebble area, especially at Sites SK-31, SK-51, SK-11 and SK-12 because these sites are in mineralized areas near the Pebble deposit. All have relatively high sulfate concentrations for the area, indicating possible contact with sulfide rock. The pH at these sites ranged from 6.2-7.2.[14]

Surface water collected in the Upper and Lower Talarik Creek (UT-01, UT-02, LT-11), Kaskanak Creek (KC-01), and South Fork Koktuli (SK-21), may be more likely influenced by organic acids. These are sites in wetlands and therefore likely to have a significant surface runoff component. The pH was 6.4 – 7.2 at each site in May 2009 and increased 0.5-1 units in June 2009 and 2010 as runoff subsided.[15] Figure 6 shows median alkalinity values and pH at all sample locations.

Changes in pH have the potential to impact aquatic life directly, and they also affect the dissolved metals concentration in streams, as more metals move into the dissolved phase as the pH decreases. This trend

[14] SK-11 was only sampled in May (pH 6.2); SK-12 and SK-31 were sampled only in June (pH 7.1, 7.2 in 2009; pH 7.0, 7.1 in 2010); SK-51 was only sampled June 2010 (pH 6.9).

[15] pH in both June 2009 and June 2010 were 0.5-1 point higher than in May 2009; LT-11 was not sampled in June 2010. Sites that were not sampled in May 2009 were not considered.

was observed with lower pH, lower alkalinity and higher metals in May 2009 during breakup, and shifting to higher pH, higher alkalinity, and lower metals in June.

Water "hardness" is attributed to calcium and magnesium concentrations. Calcium, which is generally sourced from groundwater, can moderate metal toxicity by binding to fish gills, preventing free metal ions from binding to the site. Calcium concentration will vary with surface water input; for example, the calcium concentrations are typically lower in surface water during precipitation events and will be higher when groundwater contributes more to the water chemistry in streams during the winter months or during summer low-flow periods. Sites sampled in 2009 and in June 2010 consistently recorded higher calcium concentrations in June 2010 (Figure 7).

Dissolved organic carbon can moderate metal toxicity by providing a surface for free metal ions to bind, thereby preventing the metals from binding to fish gills, fish lateral lines, or other biotic receptors. There is no clear connection between DOC and metals based on the limited data set from this study, but all the DOC concentrations were low (< 6 mg/L) at all sites during all three sampling events.

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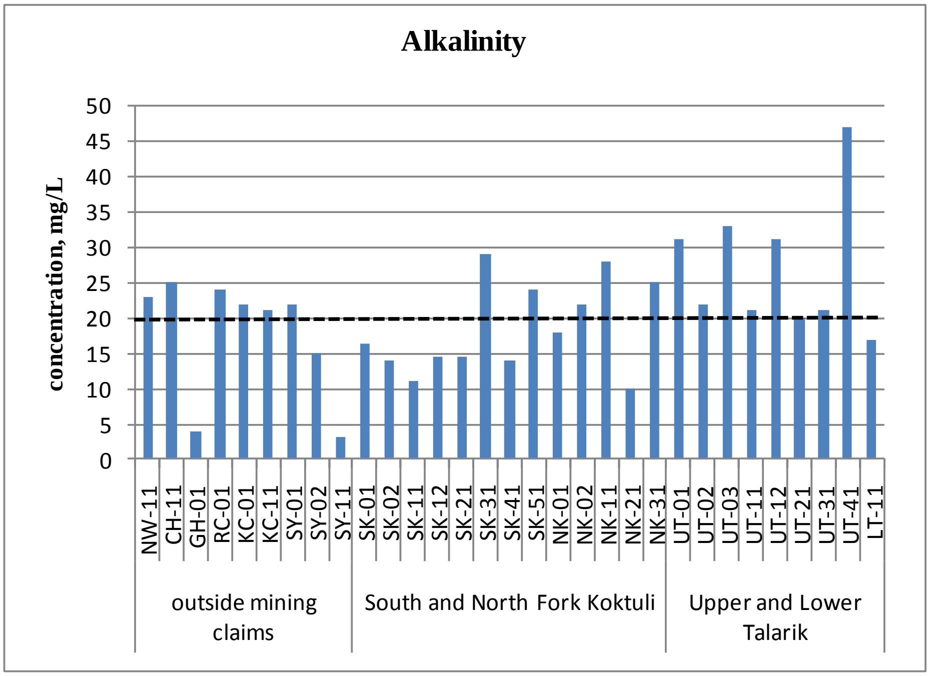
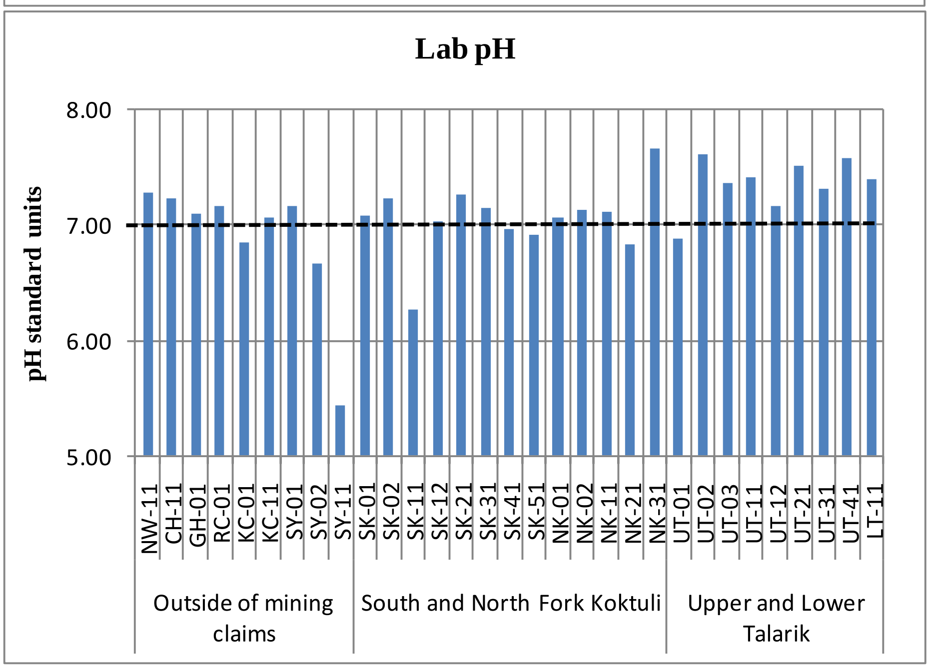


Figure 6. Median Alkalinity Concentrations and pH, Pebble Region, 2009-2010.



Notes: mg/L = milligrams per liter

Outside of mining claims refers to outside the Pebble Prospect.

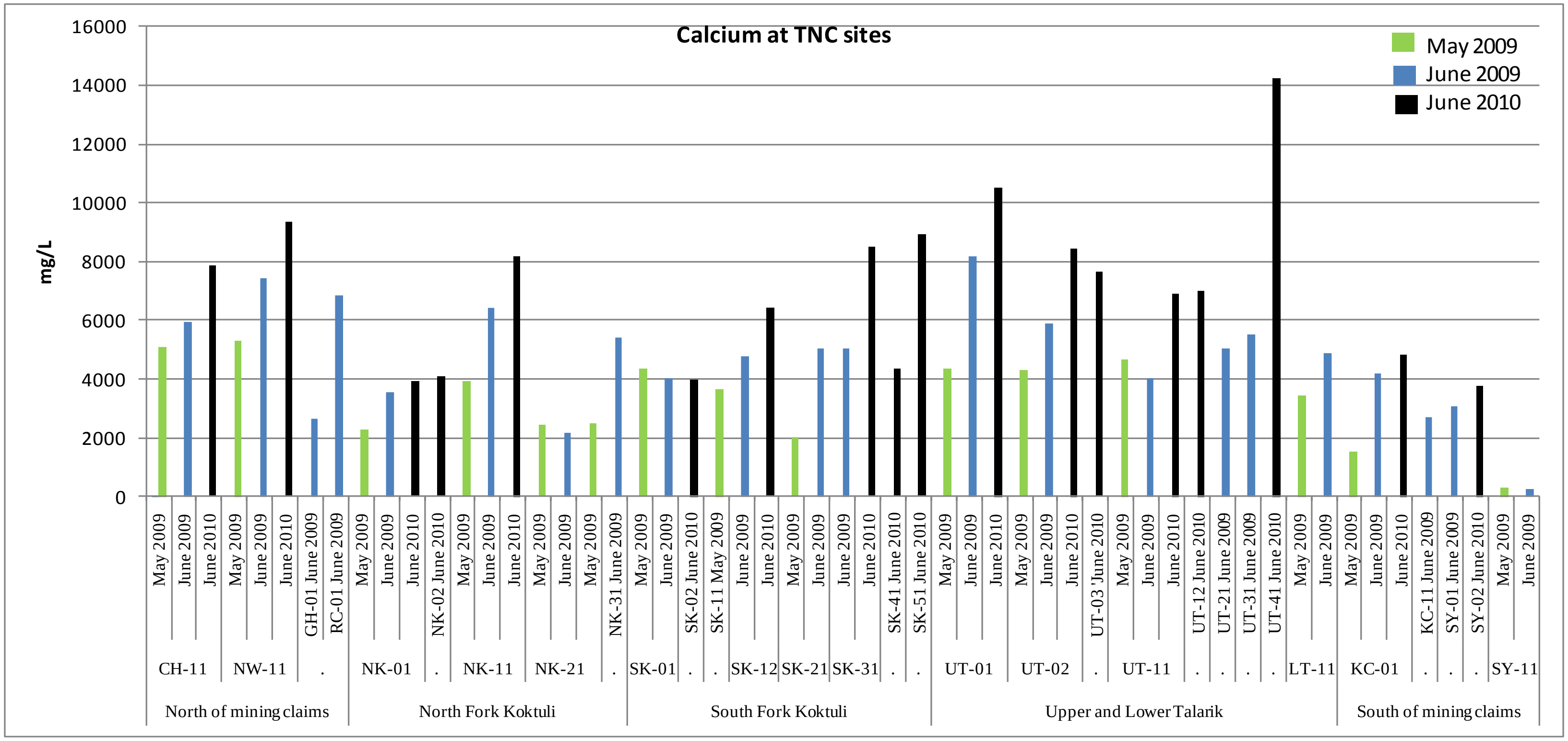


Figure 7. Calcium Concentrations Pebble Region, 2009-2010.

5.2 COMPARISON TO PLP'S DATA

The Nature Conservancy collected samples during breakup (May 2009) and in June 2009 and June 2010. These sampling events were intended to provide information on the range of parameter concentrations, with a minimal amount of sampling. The TNC samples were expected to fall within the range of the more extensive PLP data set collected between 2004 and 2007. In general, the concentration ranges from the TNC surface water samples did fall within the range of PLP data, but some medians tended to be skewed due to TNC's limited sample set and different sampling dates and times.

Other differences in sampling methodology included the 2009-2010 dissolved metal samples being filtered in the field on the stream bank, whereas the PLP samples were filtered within 12 hours after being transported back to Iliamna. This difference and the comparison of a very limited data set with the larger PLP data set may have contributed to the slight differences in metal results from the three 2009-2010 sampling events when compared to the 3-year data set compiled by PLP. Overall, the 2009-2010 data sets fell within the same concentration ranges that were measured by the PLP samples, therefore confirming the accuracy of the PLP water quality data.

Both TNC and PLP data indicate that, of the seven co-located sites, the Upper Talarik, particularly the headwaters just north of the Pebble deposit (UT100E = UT-01), had the highest alkalinity and cation concentrations and the site along the tributary draining the Kaskanak Mountain into the South Fork Koktuli had the highest sulfate concentrations (SK124A = SK-12).

A minor difference between the PLP and our 2009-2010 results was that at all the co-located sites, TNC found calcium, magnesium, sodium, and hardness concentrations lower than PLP data, with the exception that June 2010 data for the Upper Talarik Creek was similar to PLP. The DOC concentrations were higher in TNC data at most sites and aluminum was higher in TNC data, except June 2010 data which was similar to PLP results. At the co-located site closest to the Pebble deposit (i.e., SK124A = SK-12), TNC data reported higher concentrations of aluminum, arsenic, cadmium, copper, iron, lead, mercury, and zinc than PLP data.

5.3 GROUNDWATER-SURFACE WATER INTERACTIONS

The Pebble region is overlain with glacial till, and has significant groundwater-surface water interactions as reported by NDM[16]. Groundwater-surface interactions are important for salmon ecology and potential contaminant transport pathways at the Pebble site. For example, stream reaches within the Pebble region where groundwater is upwelling can provide important habitat for salmonids; the relatively constant temperatures of groundwater inputs and the tendency for upwelling zones to remain unfrozen in the winter are both situations favorable to salmon habitat. Movement of water between surface and groundwater can also transport mine-related contaminants between groundwater and surface water, increasing the likelihood of uncontrolled releases. Proposed large-scale mining activities (e.g., tailing impoundments, mine dewatering, and discharge of extracted groundwater) would likely impact the existing hydrologic system and potentially change the location, quantity, and timing of groundwater upwelling and recharge.

[16] NDM 2005; see also Wobus 2009

For this study, an attempt was made to determine whether water chemistry could be utilized to determine surface water sites with significant groundwater influence. Groundwater chemistry may differ from surface water in cation and anion concentrations, conductivity, and temperature. Major ions (e.g., calcium, magnesium, sodium, potassium, bicarbonate, and sulfate) are highest in groundwater, with the exception of sites where surface rock is high in sulfide minerals, leading to elevated sulfate in surface water. Surface water sites would be expected to have high concentrations of cations in winter when groundwater supplies most or all of the flow, and lower cation concentrations when surface runoff dilutes the groundwater inputs during spring breakup and precipitation events. Additionally, groundwater is often presumed to have constant water temperatures and have higher conductivity. Conductivity is a measure of the ability to conduct an electrical current and increases with higher concentrations of major ions, including dissolved iron and aluminum ions, and with higher water temperatures.

Major cation concentrations may inversely correlate with particulate aluminum and iron. In the study area, erosion of surface rocks contributes particulate matter to sites that tend to have high concentrations of aluminum, iron, and manganese relative to other elements. Streams fed by groundwater could be expected to have consistent high concentrations of cations and consistent low concentrations of particulate metals, while streams fed by surface runoff could see a spike in erosional metals during spring breakup, snowmelt, or storm events.

Of the 11 sites with both May and June collection data, TNC identified three as primarily groundwater fed (SK-01, UT-11, SY-11); four as mixed groundwater and surface runoff (CH-11, SK-11/12, NK-11, NK-21); and seven as primarily fed by surface runoff (NW-11, SK-21, NK-01, UT-01, UT-02, LT-11, KC-01).

Differences in calcium concentrations, conductivity, and metals at low-flow periods and high-flow periods were utilized to assess potential groundwater influence. Sites with little change in calcium concentrations between May and June were identified as having significant groundwater contributions to the surface water (Figure 8). An evaluation of changes in temperature, conductivity, and metals between sampling events was completed to help determine which TNC sites potentially have significant groundwater inputs including evaluating the following metrics:

- field conductivity with less than 15% difference between May and June
- lab specific conductance with less than 10% difference
- total aluminum concentrations with less than 20% difference between May and June

In Figure 8, sites with little change in calcium concentrations between May and June are tentatively identified as having significant groundwater contribution to the surface water. Identified sites include SK-01, SK-11, NK-21, UT-11, CH-11, and SY-11. These sites had less than 20% difference in calcium concentrations as measured in May and June 2009.

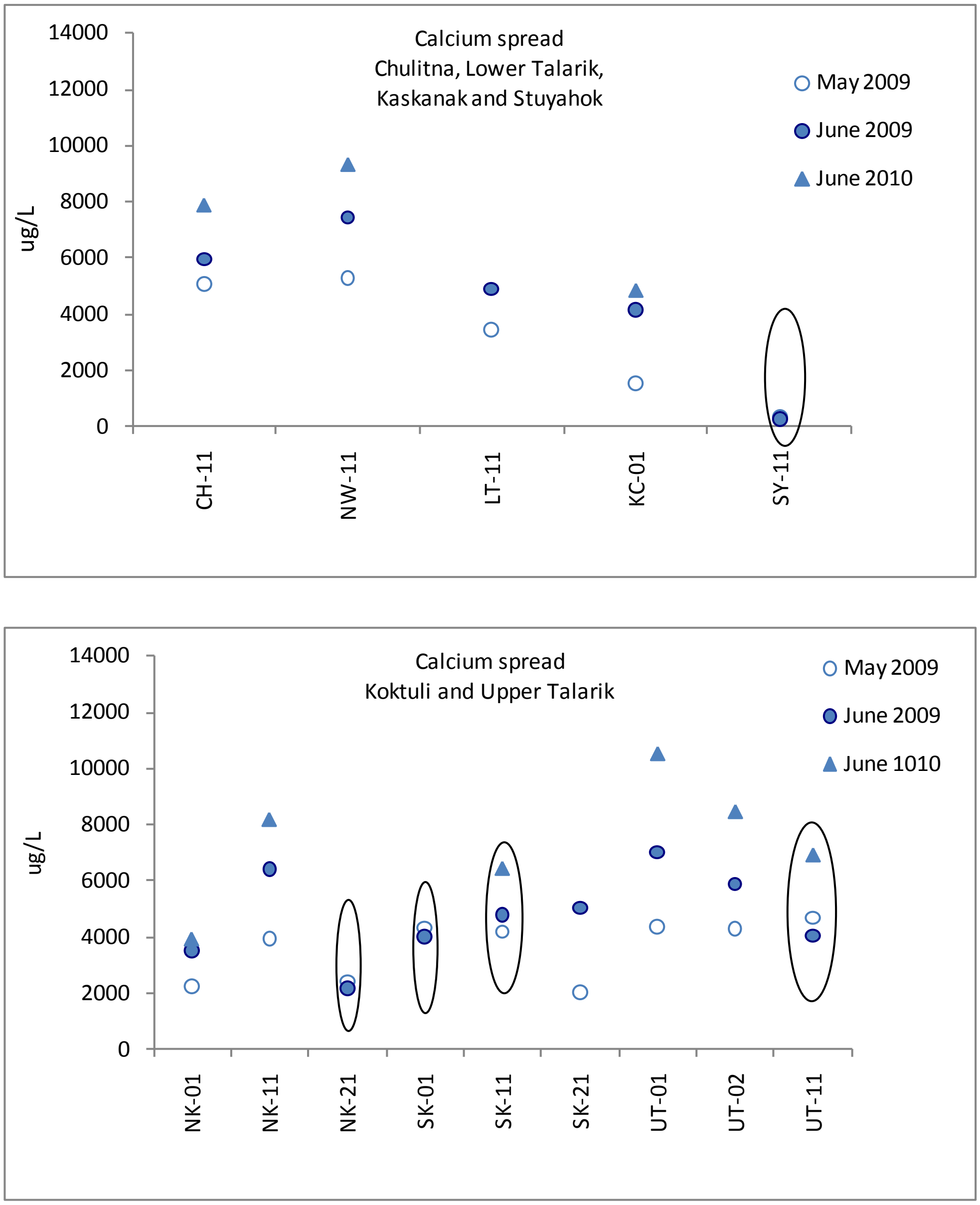


Figure 8. Groundwater-Influenced Streams Identified by Calcium Concentrations at TNC Study Sites, Pebble Region, 2009-2010.
ug/L = micrograms per liter

5.3.1 Co-Located Sites Identified With Groundwater Influence

Seven TNC sites were co-located with PLP sites, and each PLP site was evaluated for groundwater inputs using the same methods as were utilized in assessing TNC data.[17] Changes in calcium, lab-specific conductivity, and total aluminum, total manganese, and total iron were compared between winter base flow periods (February/March) and high-flow periods during breakup (late April/May) for the PLP sites sampled in 2005 -2007. These PLP sampling dates were evaluated because TNC expected that they would provide wider differences in concentrations than the May-June comparison evaluated for the TNC data (Table 10). Comparisons were made for each year; not all PLP sites had data for 2005, 2006, and 2007. Where multiple year data was available, the percent changes in each year for each parameter was averaged.

Table 10 Groundwater Indicators at TNC and PLP Co-Located Sites, Pebble Region

	Calcium, % difference		**Specific conductance, lab % difference**		**Total Aluminum, % difference**		**Total Manganese, % difference**		**Total Iron, % difference**	
Site	TNC	PLP	TNC	PLP	TNC	PLP	TNC	PLP	TNC	PLP
SK-01/ SK100B	-4%	20%	5%	40%	12%	68%	7%	86%	-7%	87%
SK-12/ SK124A	7%	24%	-5%	22%	39%	84%	19%	6%	54%	19%
NK-01/ NK100A	22%	29%	-16%	30%	56%	76%	38%	33%	30%	64%
NK-21/ NK119B	-6%	60%	-8%	38%	23%	92%	38%	19%	12%	45%
UT-01/ UT100E	23%	27%	-27%	31%	52%	69%	73%	85%	47%	78%
UT-02/ UT100B	16%	22%	-13%	20%	63%	74%	46%	36%	50%	61%
KC-01/ KC100A	47%	-30%	-41%	29%	84%	58%	38%	13%	61%	42%

Notes: Dark shading indicates small changes in parameters. These may indicate sites with strong groundwater influence. Light shading represents more change and potentially less groundwater influence. No shading indicates strong changes in parameters.

Shading on Table 10 provides a general idea of the potential contribution of groundwater to a site. The evaluation of PLP data using calcium, conductivity, and iron percent differences correlated relatively well with TNC assessments. Utilizing the difference in aluminum or iron in PLP data did not correlate well with assessing aluminum and iron changes in TNC data. The results of this evaluation are the following:

- The four co-located sites identified by TNC as fed primarily by surface runoff were also categorized as surface runoff by PLP data (NK-01, UT-01, UT-02, KC-01); all are main stem river sites. Both TNC and PLP data indicate some contribution of groundwater to NK-01 and UT-02.

[17] Field data was not available for surface water sites and could not be included in the assessment.

- Both TNC and PLP data indicate site SK-01 (PLP site SK100B) has significant groundwater influence.
- Both evaluations indicated that tributary SK-12 (PLP site SK124A) is a mix of groundwater and surface run-off; PLP data indicates it may have more groundwater input than was identified using TNC data.

Only NK-21 has conflicting assessments, with TNC data assessment identifying it as mixed waters and PLP data assessment identifying it as surface run-off.

5.3.2 PLP Sites Identified with Groundwater Influence

After analysis of co-located sites, all PLP sites were analyzed for the possibility of groundwater input. Only UT119A was placed in the groundwater-fed category (Table 11). Site UT119A has been identified by PLP as an upwelling area that likely receives groundwater from the South Fork Koktuli losing reach (near SK100C).[18]

A section of the lower South Fork Koktuli appeared to have some groundwater input (SK100B, B1, B2). Site SK100B2 may receive water returning from the SK100C losing reach (Table 11, Figure 9). The most downstream site, SK100A, also appeared to be a mix of ground and surface water, as did tributary SK124A on Kaskanak Mountain. No winter data is recorded by PLP at site SK100C, and it is presumed that this site was dry. In Figure 9, most sites have a strong differentiation between winter and breakup concentrations. When there is little difference, there may be significant groundwater input to the site; surface run-off water chemistry is likely to fluctuate seasonally more so than groundwater. Note that site SK100C had no winter data recorded and is presumed to have been a dry losing reach; SK100B2 is likely the area of upwelling downstream sites. SK100A, SK100B, and SK100B1 all have separation, but the percent change in calcium concentrations is not large and these areas may have more groundwater input than other areas of the South Fork Koktuli.

The North Fork Koktuli had no groundwater-influenced sites based on assessment of PLP data, with the possible exception of NK119B (Table 10, Figure 9). Site NK119B (TNC site NK-21) has little change in calcium in 2007, but a strong change in 2005; data is not available for 2006.

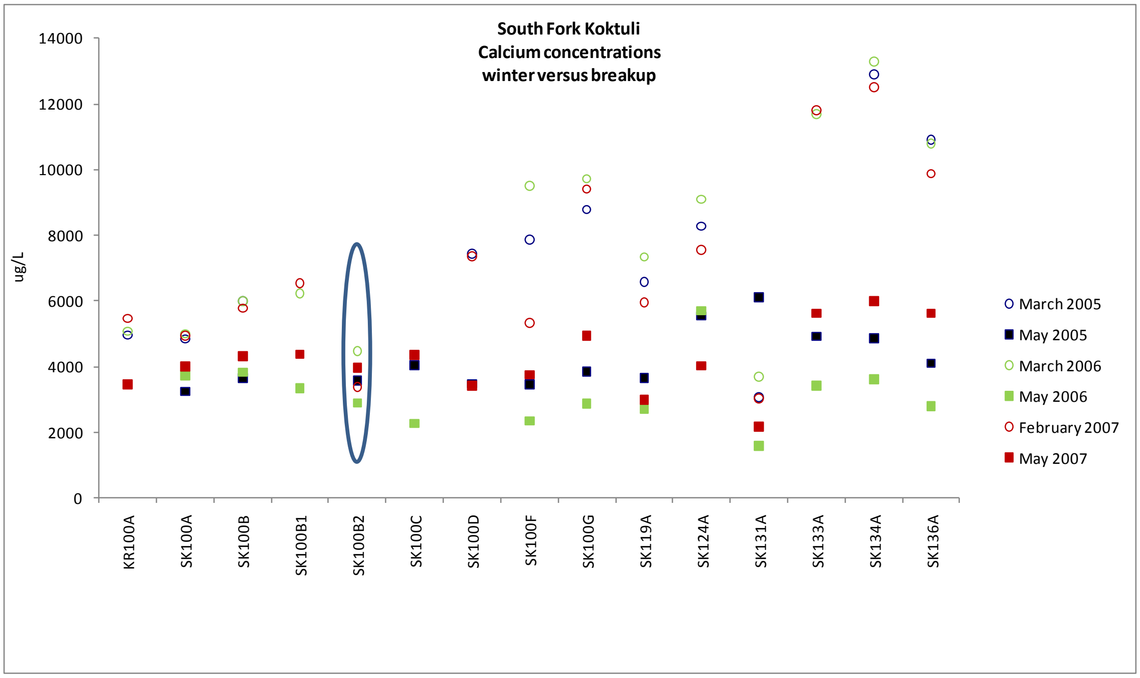
A section of the main stem of the Upper Talarik appeared to have groundwater input (UT100A, B, C, C1, and C2), as did tributary site UT135A (Table 10, Figure 10). However, this is based on limited data, as only UT100B had three years of data. In Figure 10, most sites have a strong differentiation between winter and breakup concentrations. When there is little difference, there may be significant groundwater input to the site; surface run-off water chemistry is likely to fluctuate seasonally more so than groundwater. Site UT119A is on a tributary known to receive groundwater from the South Fork Koktuli watershed and Figure 10 also suggests that it is influenced by groundwater. A map of PLP site locations is provided as Figure 11 and those sites with potential groundwater influence are shown on Figure 12.

[18] PLP 2008 Pre-Permit Report F

Table 11 Groundwater Indicators at PLP Sites, 2004-2007

		Calcium % difference	Specific Conductance, % difference	Total Aluminum, % difference	Total Manganese, % difference	Total Iron, % difference
Region	**Site**	PLP	PLP	PLP	PLP	PLP
South Fork Koktuli	SK100A	15%	15%	89%	86%	87%
	SK-01/ SK100B	20%	40%	68%	86%	87%
	SK100B1	25%	37%	74%	45%	52%
	SK100B2	15%	14%	83%	79%	93%
	SK100D	36%	35%	79%	52%	47%
	SK100F	39%	51%	86%	49%	67%
	SK100G	42%	43%	84%	36%	30%
	SK119A	36%	31%	53%	49%	47%
	SK-12/ SK124A	24%	22%	84%	6%	19%
	SK131A	30%	17%	90%	65%	90%
	SK133A	45%	39%	78%	65%	61%
	SK134A	46%	44%	81%	28%	30%
	SK136A	44%	44%	74%	15%	34%
	SK136B	-58%	48%	94%	28%	41%
North Fork Koktuli	NK-01/ NK100A	29%	30%	76%	33%	64%
	NK100B	28%	33%	77%	64%	32%
	NK100C	37%	38%	73%	40%	32%
	NK119A	40%	49%	72%	56%	55%
	NK-21/ NK119B	60%	38%	92%	19%	45%
Upper Talarik	UT100A	18%	23%	88%	47%	59%
	UT-02/ UT100B	22%	20%	74%	36%	61%
	UT100C	15%	21%	79%	36%	50%
	UT100C1	17%	24%	92%	65%	71%
	UT100C2	23%	33%	89%	65%	74%
	UT100D	36%	35%	88%	25%	62%
	UT-01/ UT100E	27%	31%	69%	85%	78%
	UT119A	9%	9%	43%	48%	31%
	UT119B	38%	42%	68%	83%	71%
	UT135A	28%	21%	61%	11%	33%
	UT138A	37%	33%	87%	13%	55%
	UT141A	38%	42%	80%	31%	38%
	UT146A	31%	55%	48%	57%	33%
Southwest of Pebble Prospect	KC-01/ KC100A	-30%	29%	58%	13%	42%
	KR100A	23%	13%	40%	27%	43%

Notes: Dark shading indicates small changes in parameters between low-flow (February-March) and high-flow (April-May) months; lighter shading indicates more change.



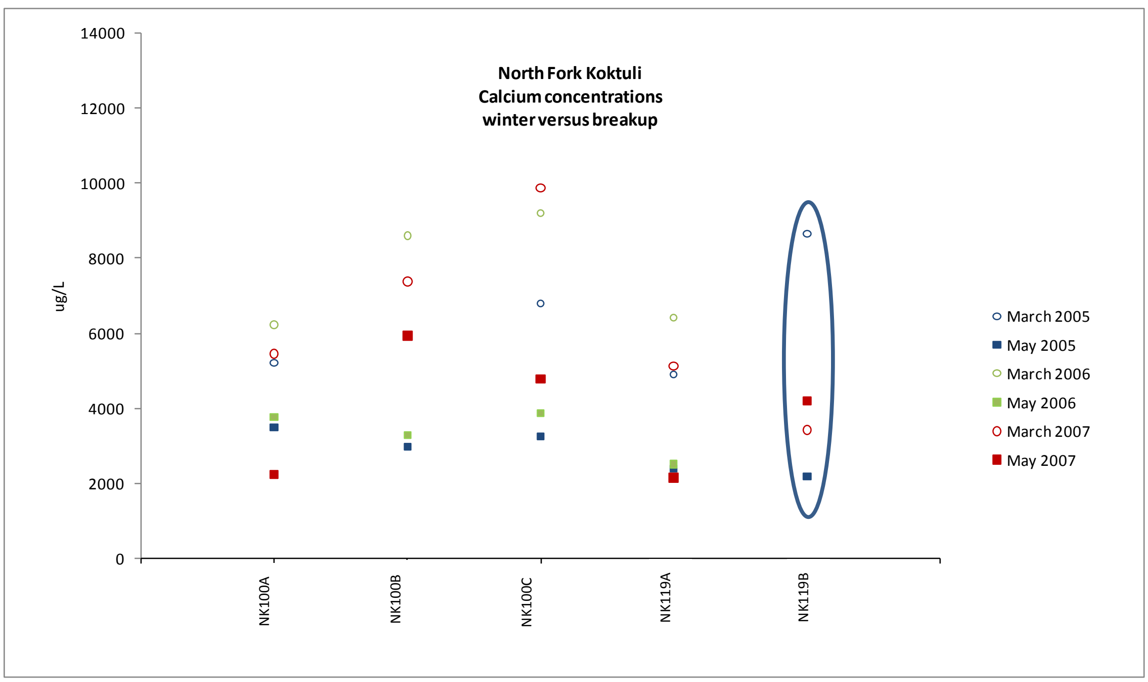


Figure 9. Calcium Concentrations at South and North Fork Koktuli PLP Sites, 2004-2007.

Circles represent concentrations during low flow and squares represent concentrations during breakup/high flow. Data is from PLP Pre-Permit Report F, Section F-2. All PLP data is preliminary and may change upon release of the final data.

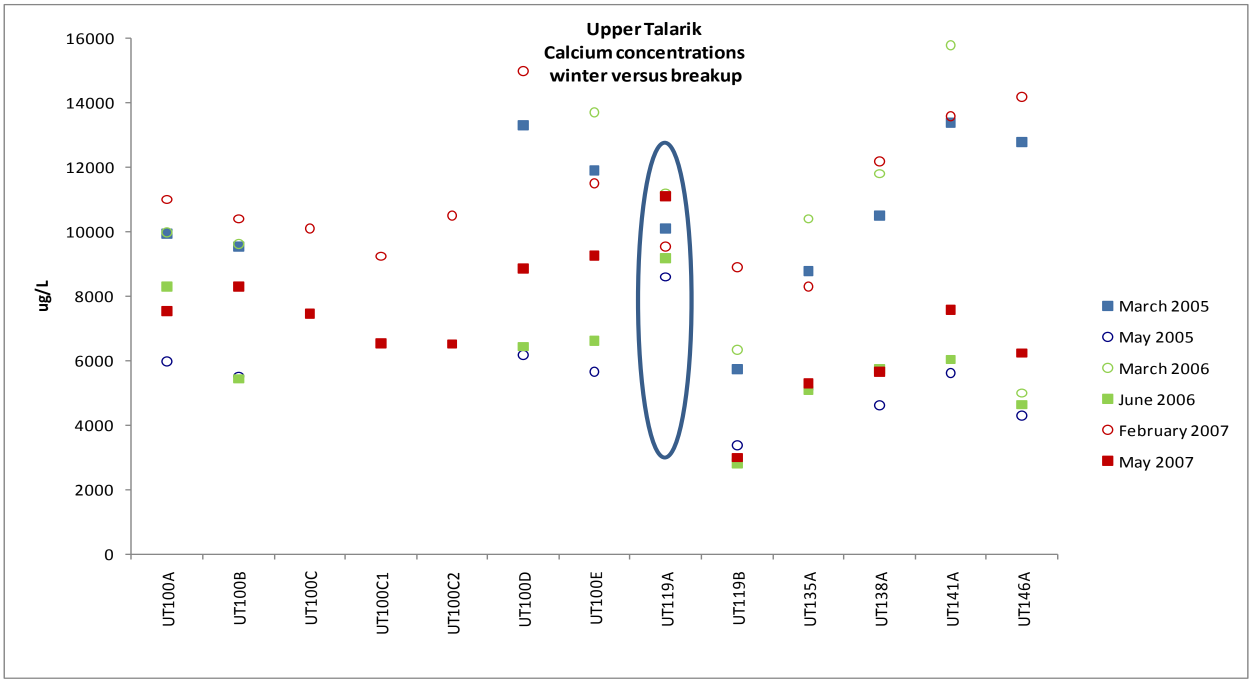


Figure 10. Calcium Concentrations at Upper Talarik PLP Sites, 2004-2007.
Circles represent concentrations during low flow and squares represent concentrations during breakup/high flow. Data is from PLP Pre-Permit Report F, Section F-2. All PLP data is preliminary and may change upon release of the final data.

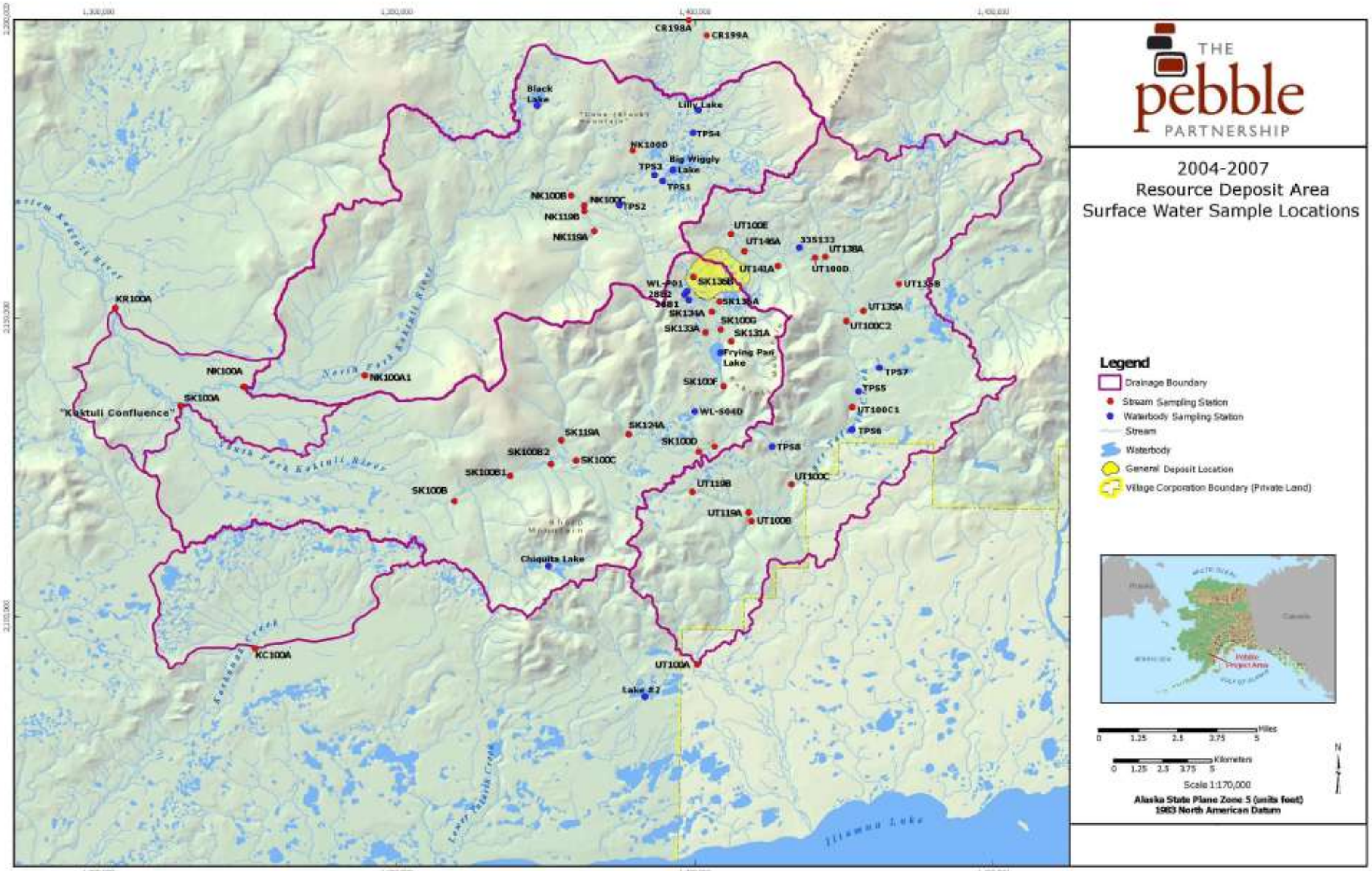


Figure 11. PLP Surface Water Sampling Sites, 2004-2007.

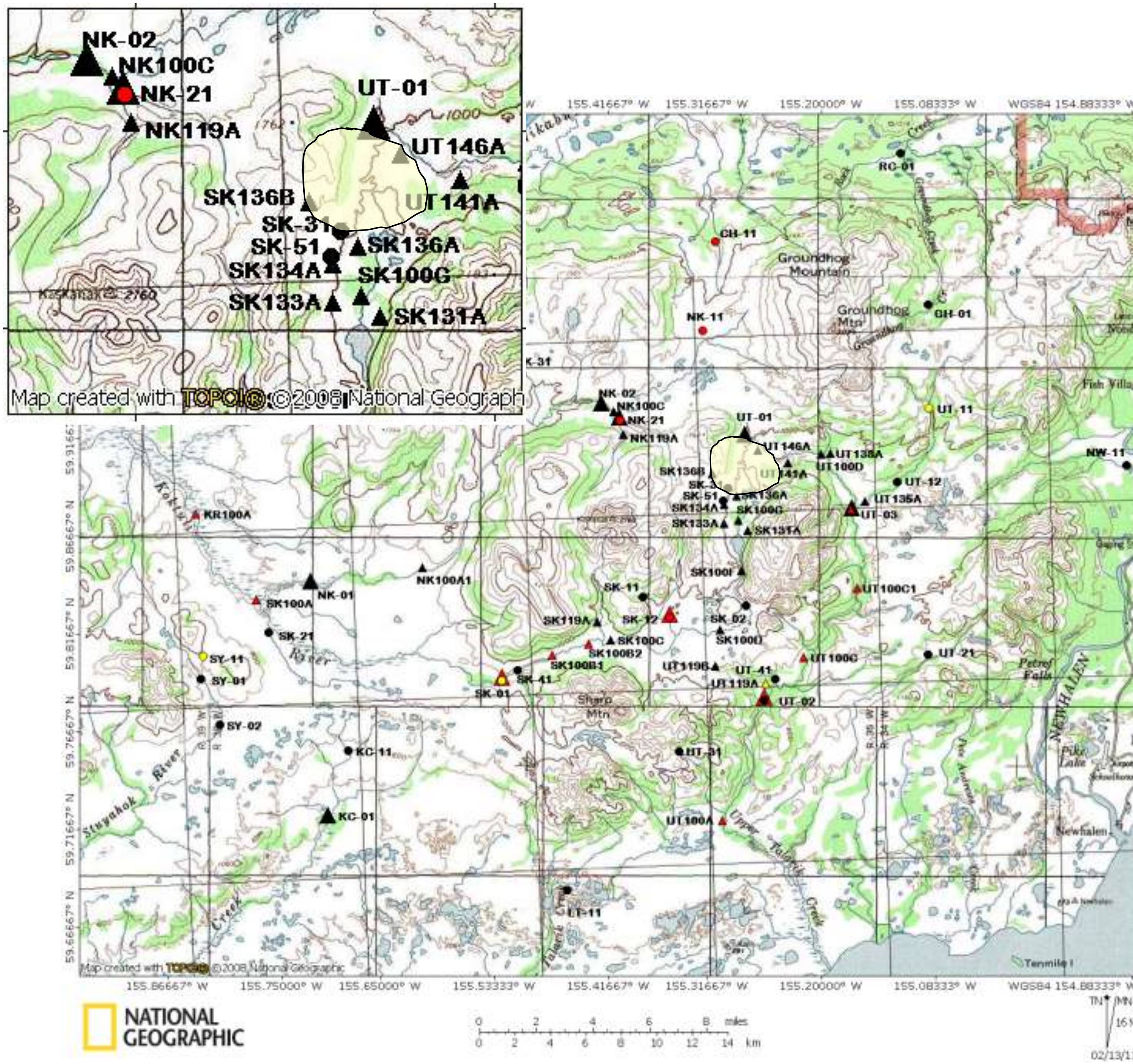


Figure 12. Potential Groundwater-Influenced Sites, Pebble Region.

Small circles – TNC sites. Small triangles – PLP sites. Large triangles – co-located sites. Yellow – strong indicator of groundwater influence, red – potentially mixed influence of groundwater and surface run-off. Where a small circle and large triangle have different colors, the small circle represents results from assessment using TNC data and the large triangle represents results from assessment of PLP data. Tan area at the headwaters of the South Fork Koktuli represents the Pebble deposit. An inset of the sites near the Pebble deposit is provided in the top left corner of the map. PLP site locations are from the document "PLP baseline hydrology stations 2004-2008: geographic coordinates 21 July 2008".

6.0 Implications

Results of this study suggest that the surface waters of this region are cold, highly oxygenated, with low buffering capacity, low metals content, very low conductivity, low DOC, and higher sediment loads during spring breakup. The low buffering capacity and low metal concentrations in the streams draining the Pebble Prospect suggest that even minor changes in water quality could adversely affect salmonid populations in three major salmon spawning and rearing drainages in the Bristol Bay/Iliamna Lake area. Without buffering, a small addition of acid would decrease stream pH rapidly. The generally low hardness and low DOC of surface waters indicated that if additional metals entered streams – through mining waste or through release from sediment as stream pH dropped – they would be bioavailable instead of being bound up to ligands or organic material.

A seasonal difference was measured between 2009 and 2010 noted by the differences in water quality between the high flow period measured in May during breakup and the lower flow periods sampled in June. The data collected in this study suggest that many of the sites sampled in May 2009 had an increase in the total concentrations of aluminum, iron, manganese, and lead above the most stringent water quality standards. The increase in particulates is due to high suspended sediment concentrations being flushed into the water column due to the significant increase in discharge caused by spring break up and increased runoff due to snowmelt. The June sampling events showed much lower metal concentrations and most metal concentrations did not exceed the water quality standards, emphasizing the low metal content of the surface water in the area after breakup, even near the Pebble deposit.

Groundwater-surface water interactions in the study area appear to be widespread based on observation of numerous seeps in the region that reflect a shallow groundwater table, measurable interbasin transfer of groundwater between the South Fork Koktuli and the Upper Talarik watersheds, numerous upwelling areas along the South Fork Koktuli River[19] and open water during late winter suggest a strong groundwater influence. Comparison of cation and metal concentrations between low flow and high flow periods also suggests numerous sites visited during this study are influenced by groundwater. Understanding existing groundwater-surface water baseline conditions is important to predicting the influence that potential large-scale mine development could have on salmonid habitat and contaminant migration pathways via groundwater-surface interactions.

Within the study area copper is a primary constituent of concern for two reasons: the Pebble deposit is primarily a copper ore body, and salmon can be negatively impacted by very small increases in concentrations of copper. Copper concentrations varied both spatially and temporally in this study but rarely did they exceed the most stringent water quality criteria. Overall, the surface water quality of the area sampled had very low metal content even very near the Pebble deposit.

[19] PLP 2008 Pre-Permit Report F

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7.0 Recommendations

Based on this study and the evaluation of the PLP data, there are a number of additional topics that should be the focus of future research:

- Surface water-groundwater interactions and interbasin transfers in the upper South Fork Koktuli and in other watersheds (e.g., Kaskanak Creek) need to be more completely characterized. Groundwater and surface water quality monitoring is recommended at collocated sites quarterly. An evaluation of the PLP groundwater and seep water quality data to compare to nearby surface water quality data is recommended to help design and implement a co-located surface water - groundwater monitoring study.
- Additional water quality monitoring and identification of the upwelling zones that remain unfrozen in the winter would be beneficial. The winter base flow period dominated by groundwater may be a limiting factor on salmonid habitat in the region, and typically lasts over 5 months from October to May. It is important to better understand the winter dynamics in the streams, so that key ecological functions can be protected from potential mine-related activites (e.g., tailings impoundments, mine dewatering, and discharge of extracted groundwater).
- Understanding the watershed ecology of the region based on evaluating and summarizing the June 2010 co-located data set that collected physical, biological, and chemical parameters (e.g., water quality, fisheries, macroinvertebrates, diatoms and algae) is important.
- A metal-loading study is recommended because the characterization of baseline water quality requires an understanding of sources that contribute metals to the streams. Metal-loading profiles use discharge measurements and synoptic water sampling to capture a snapshot of the metal loads in a stream (ideally at low-flow conditions). The mass loading pattern expressed at low flow reflects the importance of metal sources that enter the stream on a continuous basis and help to identify which sources contribute to high concentrations during the base flow periods in winter.
- Additional sampling throughout the year for DOC is recommended, given its importance to moderate metal toxicity by providing a surface for free metal ions to bind, thereby preventing the metals from binding to fish gills, fish lateral lines, or other biotic receptors.
- A survey of streams along the proposed road and port system, even one as minimal as a survey with a handheld field meter to measure temperature, dissolved oxygen, and conductivity, would be valuable.
- Continued monitoring of Kaskanak Creek and Stuyahok River and other unique streams that were sampled by TNC in 2009-2010 should strongly be considered for future monitoring.[20]

[20] Woody 2010

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