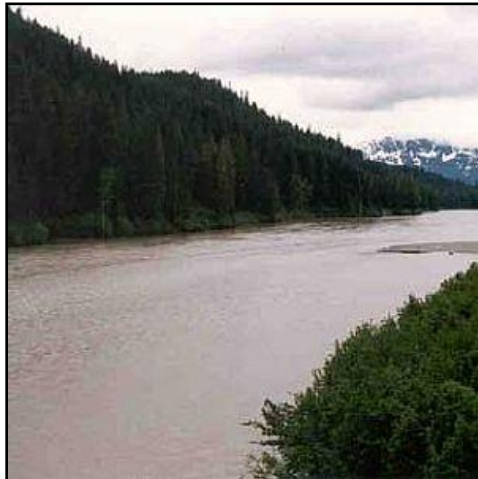


CANADA-BRITISH COLUMBIA WATER QUALITY MONITORING AGREEMENT

WATER QUALITY ASSESSMENT OF THE ISKUT RIVER BELOW JOHNSON RIVER, BRITISH COLUMBIA (1990 – 2007)



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EXECUTIVE SUMMARY

This report assesses seventeen years of water quality data from the Iskut River below Johnson River, in north-western B.C. (Figure 1). This station was established in 1980 for water quality and is currently sampled on a bi-monthly (once every two months) basis by the Water Survey of Canada when they visit the co-located hydrometric site. The Iskut joins the Stikine River 8 km downstream from the sampling site, which subsequently flows into the Alaskan panhandle and into the Pacific Ocean. Mining, and forestry to a lesser extent, are the main anthropogenic influences on the Iskut River.

CONCLUSIONS

- Water quality in the Iskut River is generally very good.
- Total cadmium, chloride, colour, fluoride and total lead had statistically significant decreasing trends over the sample period.
- Extractable calcium, extractable gallium, total manganese, total molybdenum, total suspended solids (TSS) and turbidity all had statistically significant increasing trends.
- A variety of total metal concentrations exceed aquatic life guidelines seasonally (i.e. spring freshet) but these exceedences are strongly correlated with turbidity and thus, likely bound to particulate matter and not bioavailable, and include the following:
 - Total aluminum concentrations exceeded the guidelines at times when turbidity was high. The guidelines are expressed as dissolved concentrations of the metal.
 - Total arsenic, total copper and total iron concentrations exceeded the B.C. aquatic life guidelines at times when turbidity was high.
 - Low-level total cadmium concentrations are currently near B.C. and CCME aquatic life guidelines, but these levels are considered to be natural.
 - Total chromium concentrations seasonally exceed guidelines established for Cr (VI) and Cr (III).
 - Total zinc concentrations exceeded hardness-dependent aquatic life guidelines at times when turbidity was high.

- Both turbidity and total suspended solids had statistically significant increasing trends over the sample period. Both of these parameters are generally correlated with total metals and nutrients and may result in increasing trends and concentrations in parameters related to suspended solids (i.e. total metals).
- A number of metals need to be measured differently if comparisons are to be made to guideline values as these exist. The metals and forms required to be measured are aluminum (dissolved and inorganic monomeric, when available), chromium (trivalent and hexavalent), and iron (continue to measure total but also dissolved).
- Since total metal concentrations in the Iskut River vary greatly due to freshet, it would be beneficial to measure dissolved metals in addition to total metals for guideline comparison. A new field method for collection of low-level dissolved metals is currently being developed and should be implemented in 2009 at selected sites.

RECOMMENDATIONS

It is recommended that water quality and quantity monitoring continue at the Iskut River below the Johnson River to determine trans-boundary effects between British Columbia and Alaska, to determine the effect of increasing turbidity trends on related water quality parameters and to assess the impacts of upstream activities such as mining and logging.

ACKNOWLEDGEMENTS

The data was reviewed by Ayisha Yeow and Shale Irwin, and a map of the Iskut-Stikine Basin was created by Jennifer MacDonald. This report was reviewed by Les Swain of Tri-Star Environmental, Andrea Ryan of Environment Canada and Greg Tamblyn of the B.C. Ministry of Environment. We thank these individuals for their contributions to this document. Any errors or omission are the responsibility of the author.

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INTRODUCTION

The Iskut River is located in northwest British Columbia and is the largest tributary of the Stikine River. Originating at Kinaskan Lake, the Iskut flows south and then west, where it joins the Stikine River. The Stikine River then flows out into the Alaskan panhandle 12 km downstream from the confluence and into the Pacific Ocean. The Iskut River is under ice from November to March (BWP Consulting 2003).

The water quality monitoring station is located 0.4 km below Johnson River, 8 km above the Iskut's confluence with the Stikine River, with a drainage area of 9350 km². Resource extraction activities such as mining have the greatest potential effect on water quality of all land uses in the Iskut River drainage basin. Forestry may also affect river water quality, but is not a major industry in the area due to the remote location. Finally, some commercial fisheries are located on the Iskut (BWP Consulting 2003).

Data for this report were obtained from samples collected every two months by Environment Canada between 1990 and 2007; the data are stored under ENVIRODAT station number BC08CG0001 and in the provincial EMS database under site 0920125. Water quality parameters were tested for trends and compared to B.C. guidelines. The Water Survey of Canada operates a flow gauge station at the water quality monitoring station (site number BC08CG001).

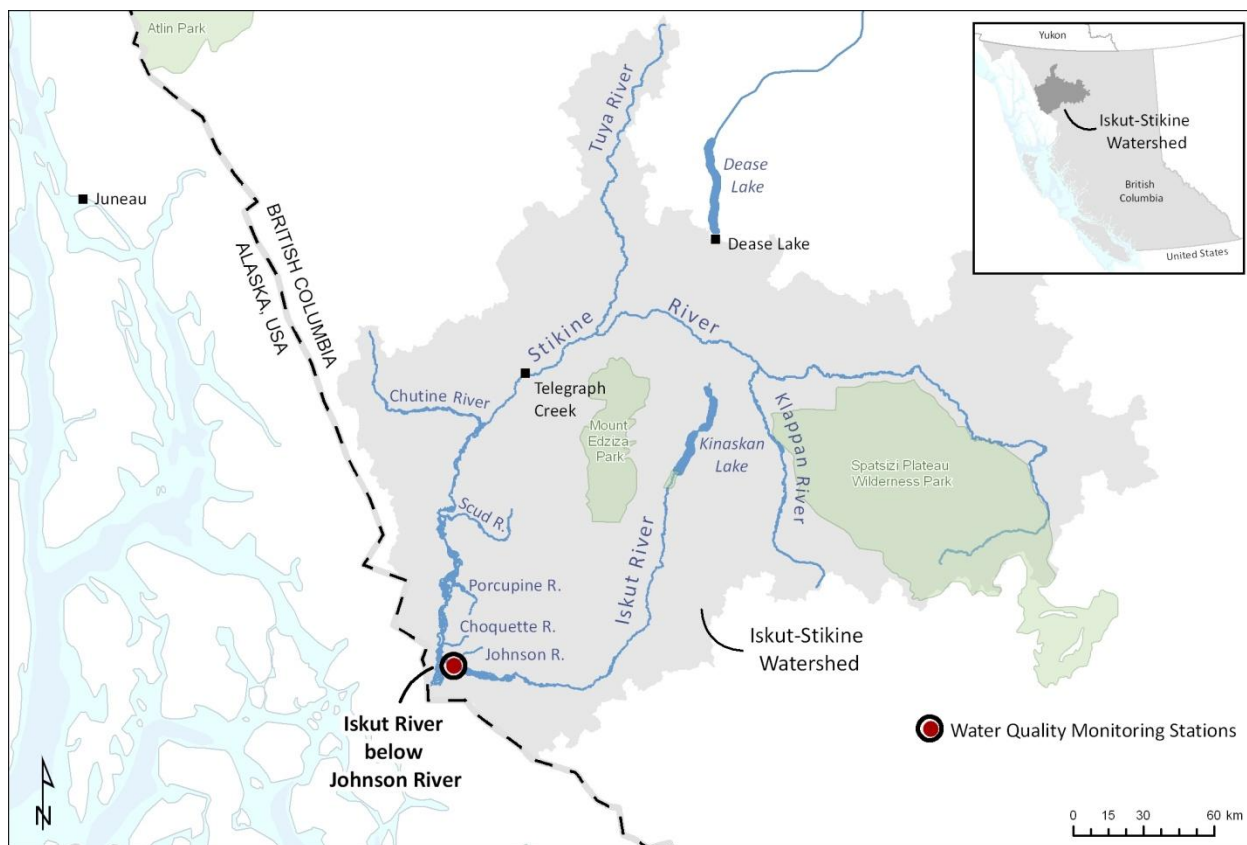


Figure 1: Map of the Iskut River.

QUALITY ASSURANCE

Efforts were taken to ensure quality control and quality assurance throughout the sample period. Duplicate or triplicate samples and field blanks were scheduled at regular intervals to assess potential sources of sample contamination and precision. The water quality results were reviewed in advance of the preparation of this report and questionable or erroneous values were removed from the dataset. Total dissolved nitrogen results were known to be contaminated between 2003 and 2005 from filters used in analyses and thus, this parameter was not considered in this report.

STATISTICS

Non-parametric statistical tests were used since most water quality parameters are not normally distributed. Time series trend analyses were conducted using the Mann-Kendall trend (MK) and the Seasonal Kendall trend tests (SK). Sen's slope estimate was used to approximate change over time.

The MK test is used to determine significant changes over time, but it cannot account for seasonal changes in a parameter, such as changing concentrations due to freshet events. To account for seasonality in the results, the SK trend test is used. Here, the data are grouped seasonally and the MK test is computed on each individual season (Helsel and Hirsh 2001). Seasonality was defined using parameters which greatly influence water quality, in this case, turbidity. The seasons used for assessment at this site were related to river discharge and included the freshet maximum (high water), rising and falling limbs, and baseflow. Spearman Rank Correlation was used to determine parameters that can be defined by turbidity seasonality, and then tested using the Kruskal-Wallis test. Parameters which had significant seasonal differences were further test for trends using the SK trend test.

Mann-Kendall and Seasonal Kendal trend tests were also flow-adjusted when tested parameters were highly correlated with flow. For example, major ions are often diluted during high flows (freshet) and concentrated during base flows when groundwater inputs provide the main source of flow and thus, they are often negatively correlated with flow. Flow adjustments were conducting using WQStat Plus™. This program assumes log-linear relationships between discharge (flow) and related parameters, and linear regressions are conducted to model the effect of flow on test parameters. Residuals from these linear regressions were subsequently tested for trends using the MK and SK test.

WATER QUALITY ASSESSMENT

The state of the water quality was determined by comparing the results to the B.C. Environment's *Approved Water Quality Guidelines* (Nagpal *et al.* 2006a) and *Working Criteria for Water Quality* (Nagpal *et al.* 2006b), and the *Canadian Council of Ministers of the Environment Guidelines for the Protection of Aquatic Life Guidelines* (2007). No site-specific water quality objectives have been developed for this portion of the Iskut River. Substances not discussed below met or rarely exceeded guidelines and displayed no significant trends during the sample period and include the following: alkalinity, antimony, barium, beryllium, bismuth, boron, dissolved bromide, dissolved organic carbon, total organic carbon, cobalt, cyanide, total hardness, extractable lanthanum, lithium, magnesium, nickel, nitrate, pH, phosphorus, potassium, TDS, extractable rubidium, selenium, dissolved silica, silver, sodium, specific conductance, strontium, dissolved sulphate, water temperature, thallium, tin, extractable uranium and vanadium.

Parameters with significant increasing or decreasing trends are outlined below and summarized in Table 1. Parameters which exceeded guidelines are described below.

Table 1: Mann-Kendall and Seasonal Kendall results with Sen’s Slope Estimation for parameters with statistically significant trends.

Parameter	Mann Kendall (Flow-Transformed)		Seasonal Kendall (Flow-Transformed)	
	<i>P</i> -value	Slope (units a ⁻¹)	<i>P</i> -value	Slope (units a ⁻¹)
Cadmium, Total (µg L ⁻¹)*	<0.01 [†]	-0.02	<0.05 [†]	-0.02
Calcium, Extractable (mg L ⁻¹)	<0.05 [†]	0.25	<0.05 [†]	0.23
Chloride (mg L ⁻¹)	<0.01 [†]	-0.04	<0.05 [†]	-0.04
Colour (units)	<0.01 [†]	-0.63	<0.05 [†]	-0.52
Fluoride (mg L ⁻¹)	<0.01	-0.004	na	na
Gallium, Extractable (µg L ⁻¹)	<0.05 [†]	0.02	<0.05 [†]	0.02
Lead, Total (µg L ⁻¹)	<0.05 [†]	-0.03	ns	na
Manganese, Total (µg L ⁻¹)	<0.05 [†]	1.98	<0.05 [†]	1.94
Molybdenum, Total (µg L ⁻¹)	<0.05 [†]	0.01	ns	na
TSS (mg L ⁻¹)	<0.01 [†]	4.63	<0.05 [†]	4.31
Turbidity (NTU)	<0.01 [†]	1.14	<0.05 [†]	1.07

*Decrease likely due to changing MDLs

[†]Flow-adjusted

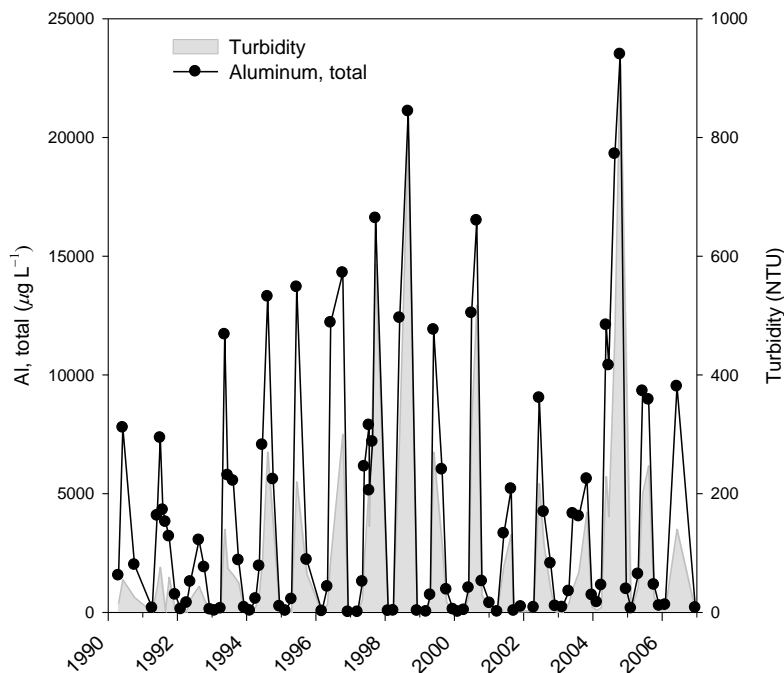
ns, non-significant

na, not applicable

Aluminum: Total aluminum varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.92$; Figure 2). Current B.C. water quality guidelines are established for dissolved aluminum and cannot be directly compared to total aluminum concentrations. Total aluminum concentrations often exceed the B.C. aquatic life guideline for dissolved aluminum (maximum $100 \mu\text{g L}^{-1}$) and the CCME guideline for total aluminum ($100 \mu\text{g L}^{-1}$). However, since these seasonal spikes are highly correlated with turbidity, they are likely bound with particulate matter and not biologically available.

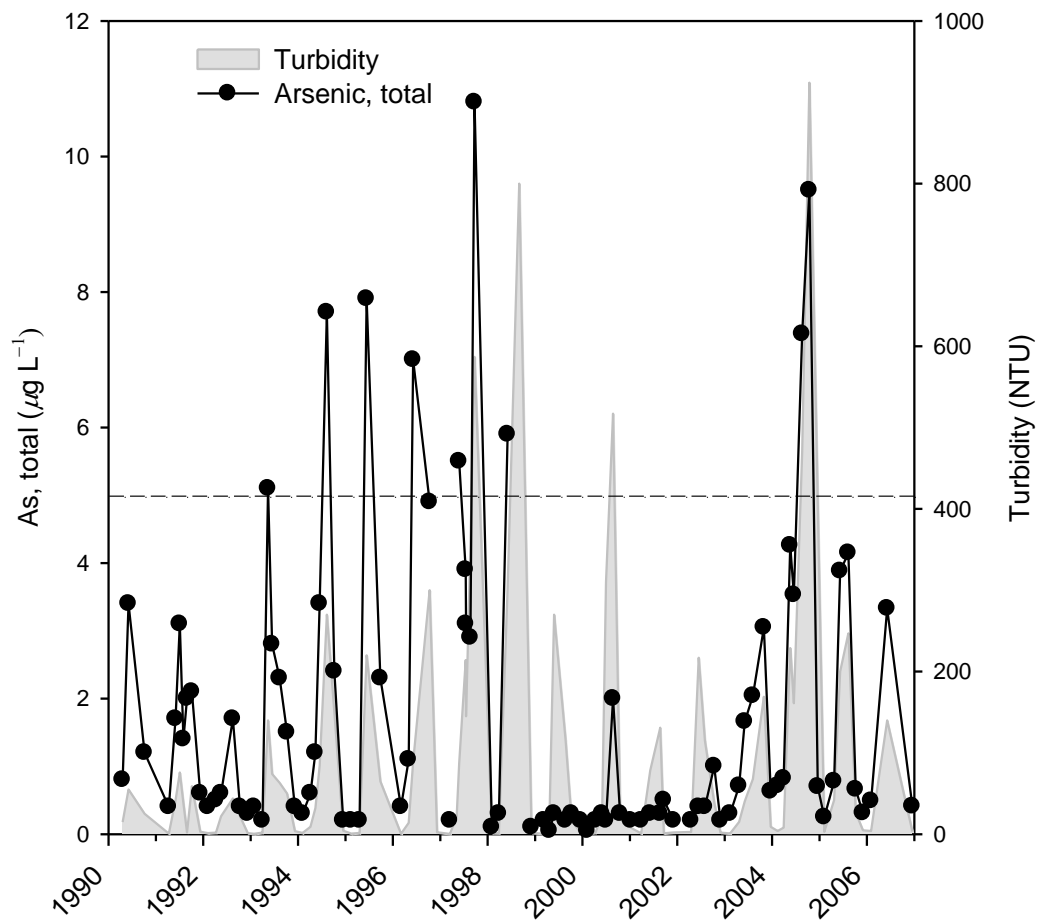
In order to make direct comparison to guidelines, aluminum should be measured as the dissolved fraction. Also, the CCME (2005 draft) are considering revising the aluminum guideline to protect aquatic life to the inorganic monomeric form; however, at present, few laboratories have the capability to measure this form.

Figure 2: Total aluminum concentrations and turbidity measurements in the Iskut River from 1990 to 2007.



Arsenic: Total arsenic varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.70$; Figure 3). The current maximum B.C. aquatic life guideline for total arsenic is a maximum of $5 \mu\text{g L}^{-1}$ and is exceeded periodically during high turbidity events. However, since these seasonal spikes are highly correlated with turbidity, the total arsenic concentrations are likely bound with particulate matter and not biologically available.

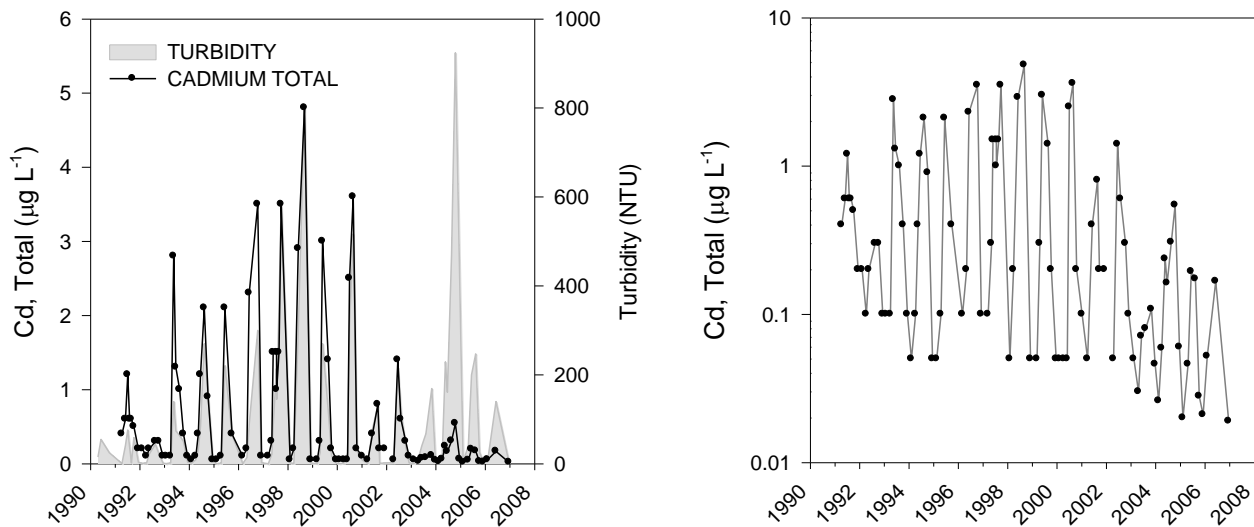
Figure 3: Total arsenic concentrations and turbidity measurements in the Iskut River from 1990 to 2007.



Note: Dashed line denotes the B.C. aquatic life guideline for total arsenic.

Cadmium: Total cadmium varies greatly seasonally and is strongly correlated with turbidity (Spearman Correlation, $r_s = 0.64$; Figure 4) suggesting that the spikes are related to particulate matter. Both MK and SK tests resulted in significant negative trends (MK, $p < 0.01$; SK, $p < 0.05$, slope = $-0.02 \mu\text{g L}^{-1} \text{ a}^{-1}$; Table 1). However, lowering laboratory detection limits over time have likely interfered with the statistical analyses (see Figure 4, total cadmium log-scale over time) and therefore, we cannot conclude that total cadmium concentrations have been significantly decreasing since 1990. Current cadmium guidelines are near or above the CCME aquatic life guideline ($0.017 \mu\text{g L}^{-1}$), and near or below the hardness-dependent B.C. working aquatic guideline which ranged between $0.01 \mu\text{g L}^{-1}$ and $0.04 \mu\text{g L}^{-1}$ over the sample period.

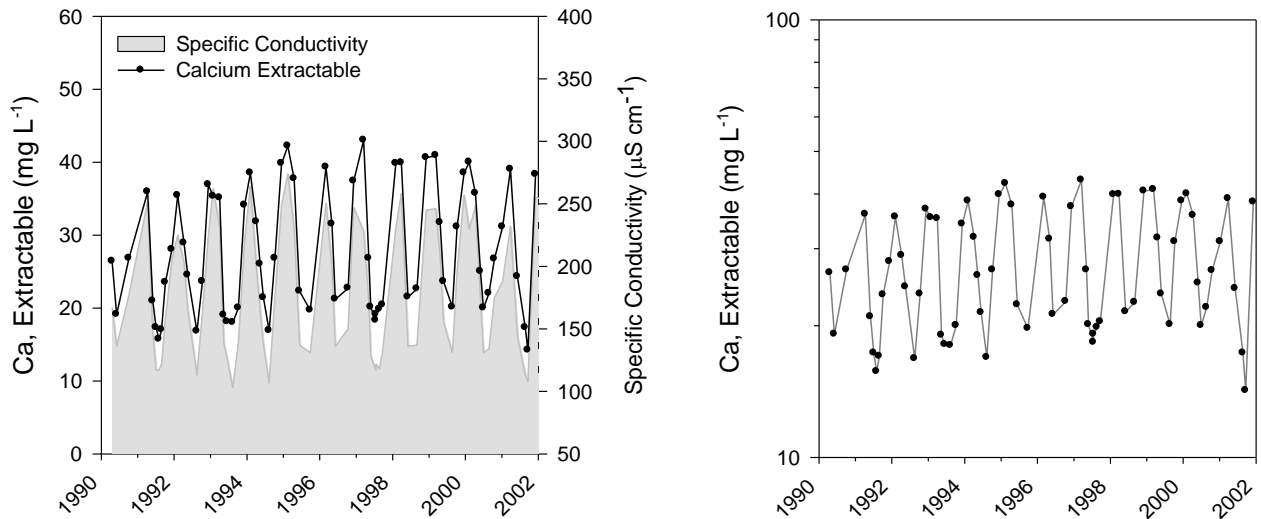
Figure 4: Total cadmium and turbidity (left) and log-scale total cadmium measurements (right) in the Iskut River from 1990 to 2007.



Calcium: Calcium, measured as extractable calcium, was sampled from 1990 to 2002.

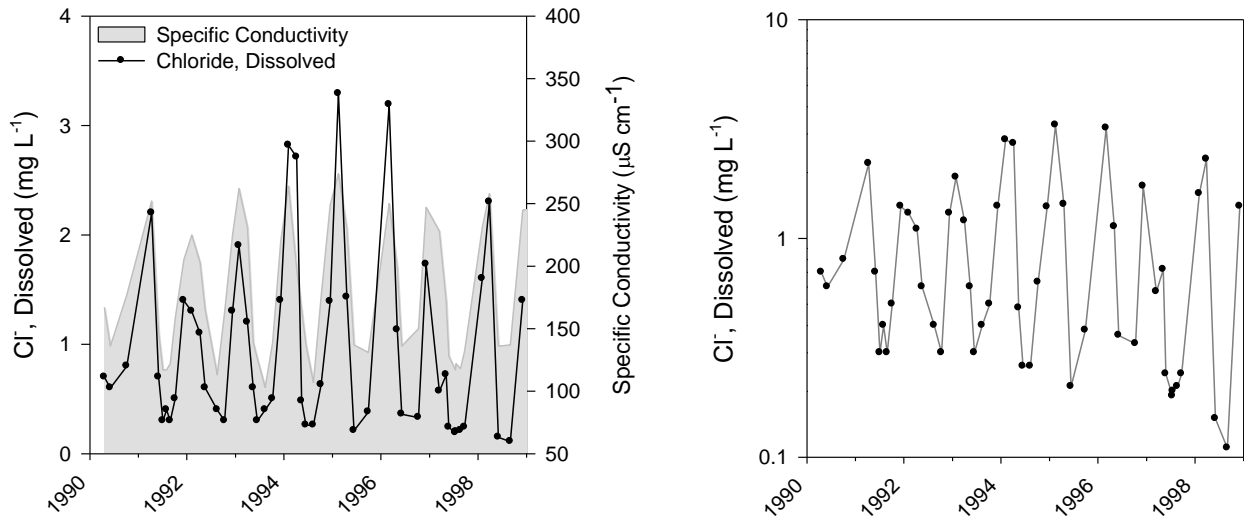
Extractable calcium concentrations significantly increased over the sample period (MK test, $p < 0.05$, slope = $0.25 \text{ mg L}^{-1} \text{ a}^{-1}$; SK test, $p < 0.05$, slope = $0.23 \text{ mg L}^{-1} \text{ a}^{-1}$; Table 1). The B.C. working water quality guidelines are established to determine the sensitivity of water bodies to acid inputs, and current calcium concentrations suggest that the Iskut River has low sensitivity to acid inputs.

Figure 5: Extractable calcium concentrations from 1990 to 2002.



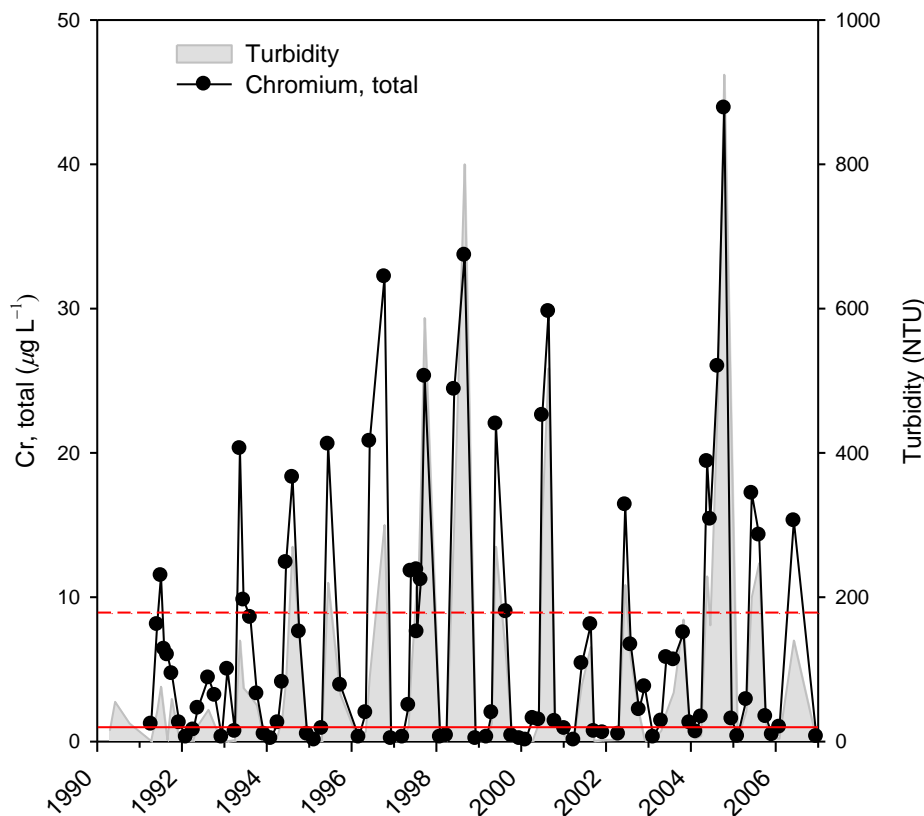
Chloride: Dissolved chloride concentrations were measured from 1990 to 1999 and had a statistically significant decreasing trend during this time (MK, $p < 0.01$, slope = $-0.04 \text{ mg L}^{-1} \text{ a}^{-1}$; SK, $p < 0.05$, slope = $-0.04 \text{ mg L}^{-1} \text{ a}^{-1}$; Table 1). However this trend should be viewed with caution as only eight years of data were available for assessment. Dissolved chloride concentrations are well below the B.C. aquatic life guideline of 600 mg L^{-1} .

Figure 6: Dissolved chloride concentrations were measured from 1990 to 1999.



Chromium: Total chromium varies greatly seasonally and is strongly correlated with turbidity (Spearman Correlation, $r_s = 0.87$; Figure 7) suggesting that spikes are related to suspended sediments. The current B.C. (and CCME) working water quality guideline for aquatic life for chromium is $1 \mu\text{g L}^{-1}$ (Cr VI) and $8.9 \mu\text{g L}^{-1}$ (Cr III). Although not directly comparable, total chromium exceeds these guidelines seasonally; these exceedences are largely associated with particulate matter and unlikely available for biological uptake. Efforts should be made to measure both forms of chromium (Cr VI and Cr III) so that comparisons to the guidelines are possible.

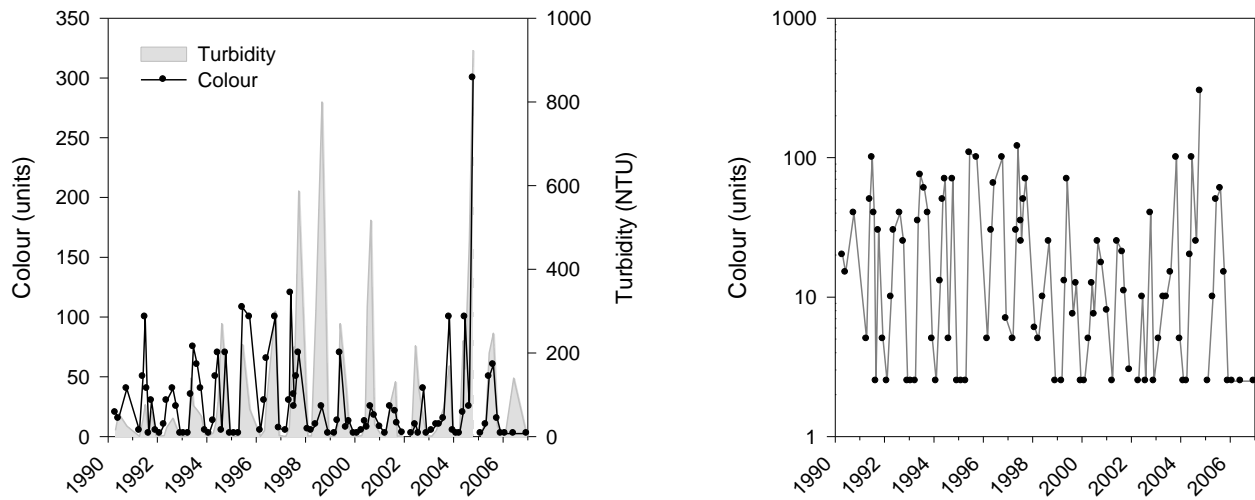
Figure 7: Total chromium concentrations in the Iskut River from 1990 to 2007.



Note: The solid red line represent the B.C. and CCME working aquatic life guideline for Cr (VI) and the dashed red line represent the B.C. working aquatic life guideline for Cr (III)

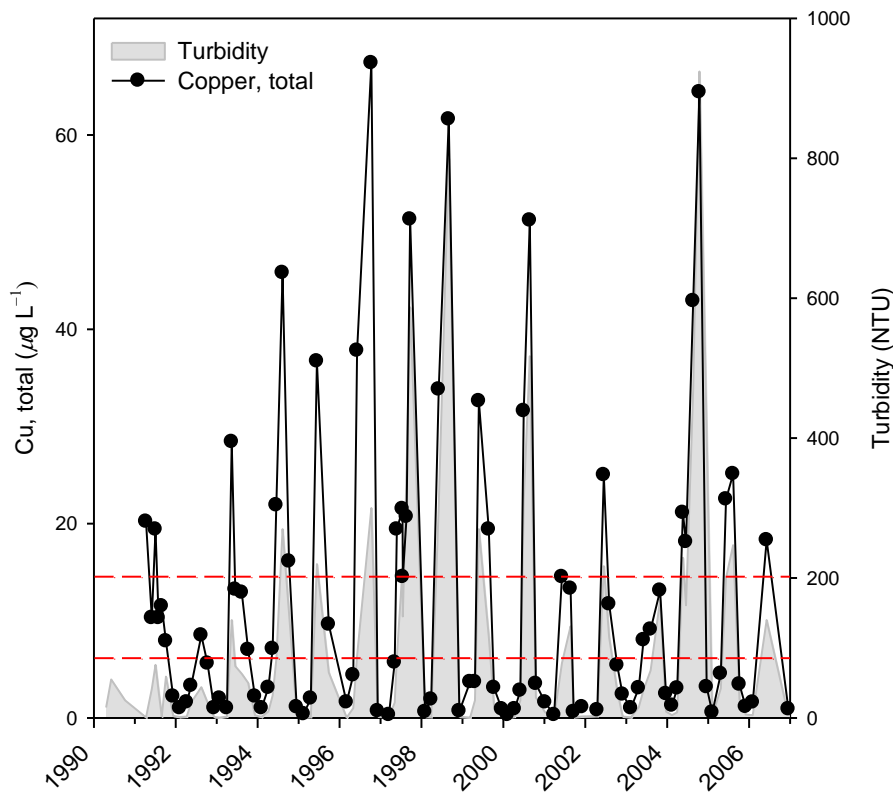
Colour: Colour was measured as apparent colour from 1990 to 1997 and true colour from 1998 to 2007. Colour measurements were strongly correlated with turbidity (Spearman Correlation $r_s = 0.76$) and mean daily flow (Spearman Correlation $r_s = 0.71$), suggesting that seasonal spikes are associated with freshet events. Colour concentrations have been significantly decreasing (MK, $p < 0.01$, slope = -0.63 units a^{-1} ; SK, $p < 0.05$, slope = -0.52 units a^{-1} ; Table 1) since 1990.

Figure 8: Colour and turbidity measurements (left) and log-scale colour measurements (right) in the Iskut River from 1990 to 2007.



Copper: Total copper varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.84$; Figure 9). The current B.C. aquatic life guideline for total copper is hardness-dependent and ranged between $6 \mu\text{g L}^{-1}$ and $15 \mu\text{g L}^{-1}$ (median = $9.7 \mu\text{g L}^{-1}$) over the sample period. This guideline was exceeded over the sample period during high turbidity events (freshet). However, since these seasonal spikes are highly correlated with turbidity, the total copper concentrations are likely bound with particulate matter and not biologically available.

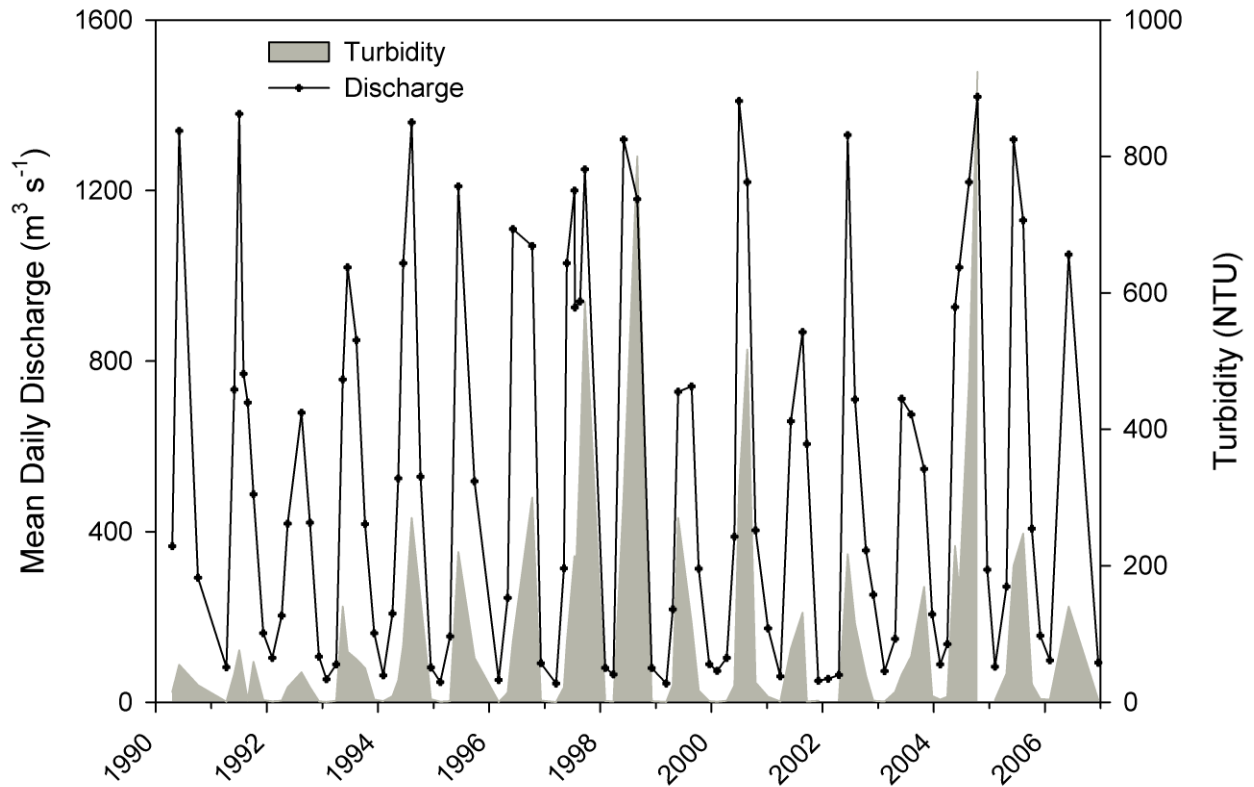
Figure 9: Total copper and turbidity measurements in the Iskut River from 1990 to 2007.



Note: Dashed red lines denote the minimum and maximum total copper thresholds calculated over the sample period.

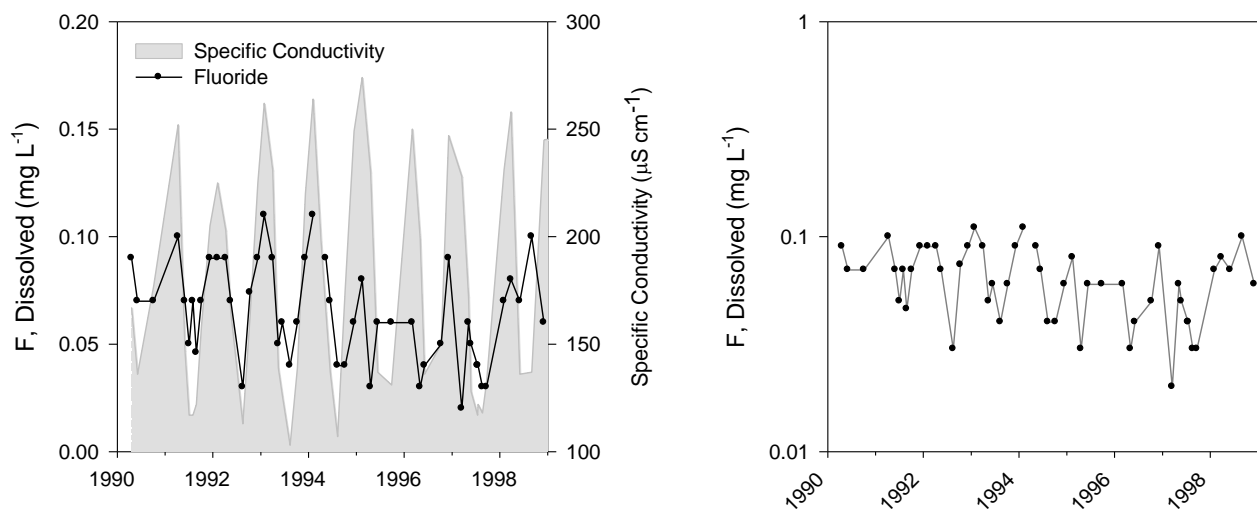
Flow: Discharge is measured by a collocated Water Survey of Canada site. Mean daily discharge is positively correlated with turbidity (Spearman Correlation, $r_s = 0.71$; Figure 10) and TSS (Spearman Correlation, $r_s = 0.83$) and affects the seasonal concentrations of many parameters, particularly those measured as total rather than dissolved portions. No statistically significant trends were detected.

Figure 10: Mean daily discharge and corresponding turbidity measurements from the Iskut River from 1990 to 2007.



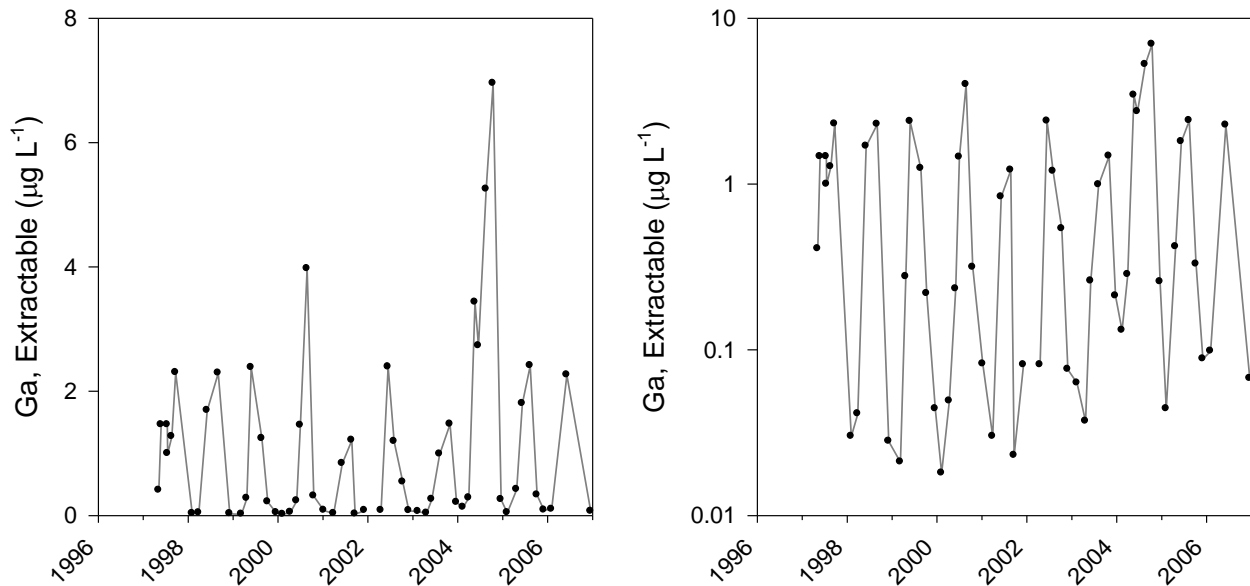
Fluoride: Dissolved fluoride concentrations were measured from 1990 to 1999 and had a statistically significant decreasing trend during this time (MK, $p < 0.01$, slope = $-0.004 \text{ mg L}^{-1} \text{ a}^{-1}$; Table 1; Figure 11). Current dissolved fluoride concentrations are well below the B.C. aquatic life guideline of 0.3 mg L^{-1} in waterbodies with total hardness greater than 50 mg L^{-1} .

Figure 11: Dissolved fluoride concentrations in the Iskut River from 1990 to 1999.



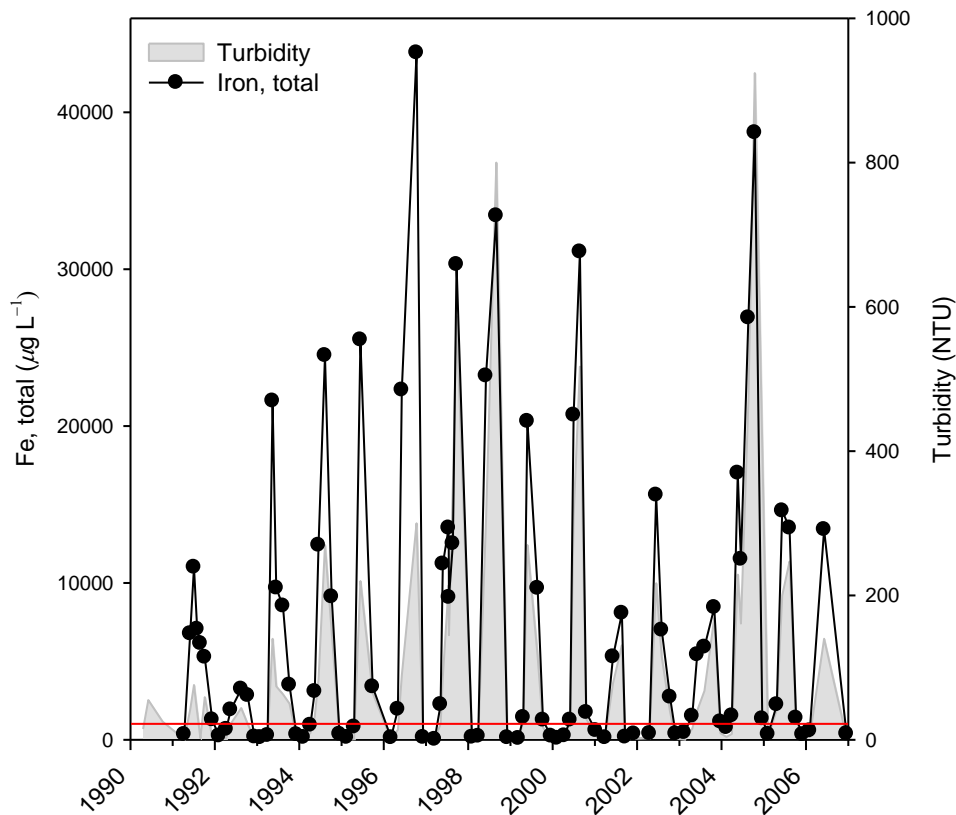
Gallium: Extractable gallium concentrations were measured in the Iskut River from 1997 to 2007 and had a statistically significant increasing trend during this time (MK and SK test, $p < 0.05$, slope = $0.02 \mu\text{g L}^{-1} \text{a}^{-1}$; Table 1). There are currently no approved or working water quality guidelines in B.C. for gallium.

Figure 12: Extractable gallium normal (left) and log-scale (right) concentrations in the Iskut River from 1997 to 2007.



Iron: Total iron concentrations have been measured in the Iskut River since 1991. Total iron has a strong positive relationship with turbidity (Spearman Correlation, $r_s = 0.91$; Figure 13). The current B.C. approved aquatic life guideline for total iron is 1 mg L^{-1} and the CCME aquatic life guideline for total iron is 0.3 mg L^{-1} ; these guideline are exceeded seasonally (freshet). However, since these seasonal spikes are highly correlated with turbidity, total iron concentrations are likely associated with suspended sediment and are not likely bioavailable.

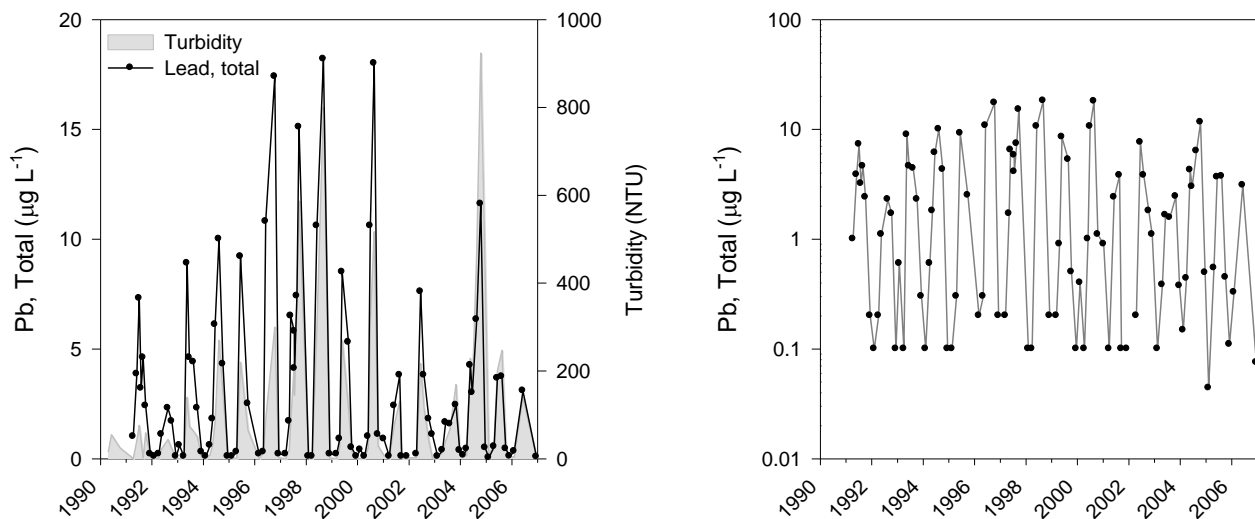
Figure 13: Total iron and turbidity measurements in the Iskut River from 1991 to 2007.



Note: Red line denotes the B.C. aquatic life guideline for total iron.

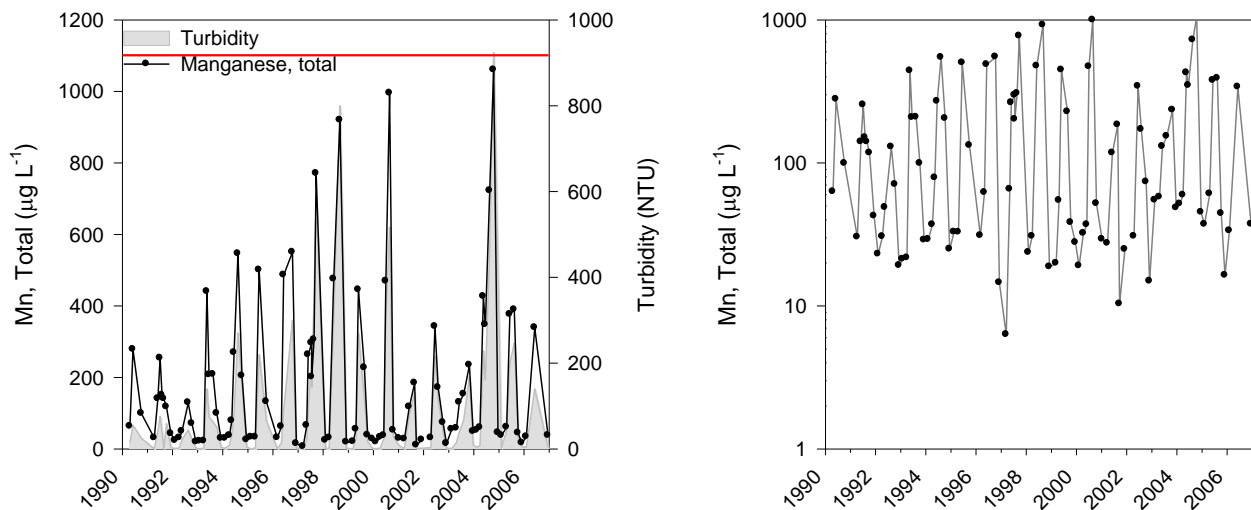
Lead: Total lead concentrations were measured in the Iskut River from 1991 to 2007 and had a statistically significant decreasing trend during this time (MK test, $p < 0.05$, slope = $-0.03 \mu\text{g L}^{-1} \text{a}^{-1}$; Table 1), although lowering detection limits may have interfered with our statistically analysis. Current B.C. aquatic life guidelines for total lead are hardness-dependent, and the minimum calculated threshold during the sample period was $20 \mu\text{g L}^{-1}$ which is higher than the total lead concentrations measured during the sample period; however, the more restrictive CCME aquatic life – a hardness-dependent guideline which ranged between 1 and $4 \mu\text{g L}^{-1}$ over the sample period - is typically exceeded during freshet.

Figure 14: Total lead and turbidity measurements (left) and log-scale total lead concentrations (right) in the Iskut River from 1991 to 2007.



Manganese: Total manganese concentrations have been measured since 1990 and are positively correlated to turbidity (Spearman Correlation, $r_s = 0.89$; Figure 15). Total manganese concentrations have been positively increasing in the Iskut River since 1990 (MK test, $p < 0.05$, slope = $1.98 \mu\text{g L}^{-1} \text{a}^{-1}$; SK test, $p < 0.05$, slope = $1.94 \mu\text{g L}^{-1} \text{a}^{-1}$; Table 1). Manganese concentrations vary greatly and during periods of high turbidity approach the B.C. acute aquatic life guideline of 1.1 mg L^{-1} (hardness-dependent guideline; Figure 15). Since total manganese concentrations are closely related to turbidity, elevated concentrations are likely associated with particulate matter and not bioavailable.

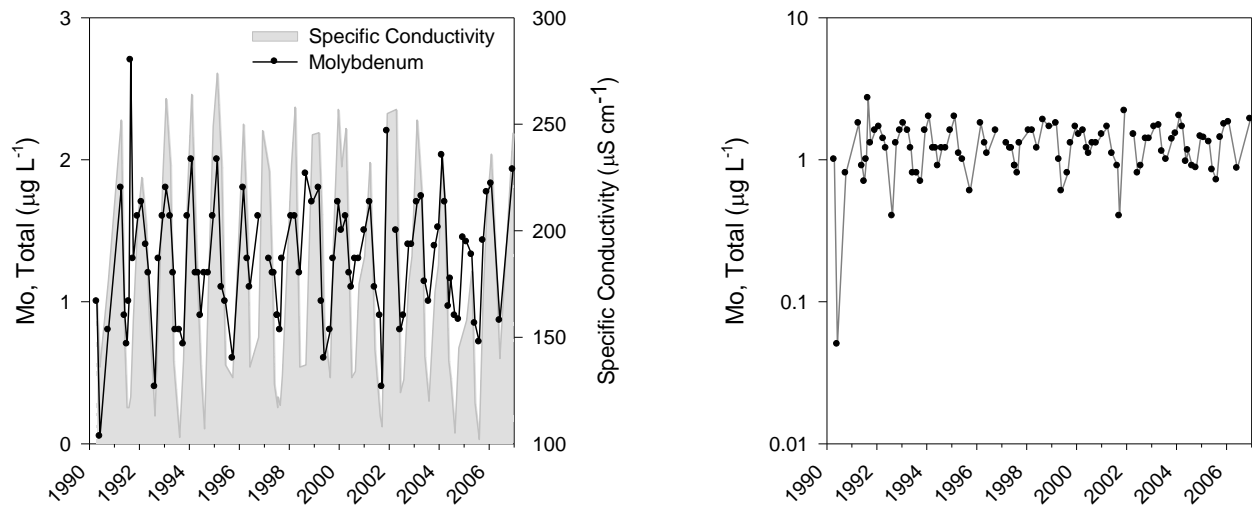
Figure 15: Total manganese and turbidity measurements (left) and log-scale total manganese concentrations (right) in the Iskut River from 1990 to 2007.



Note: Red line denotes the B.C. aquatic life guideline for total manganese.

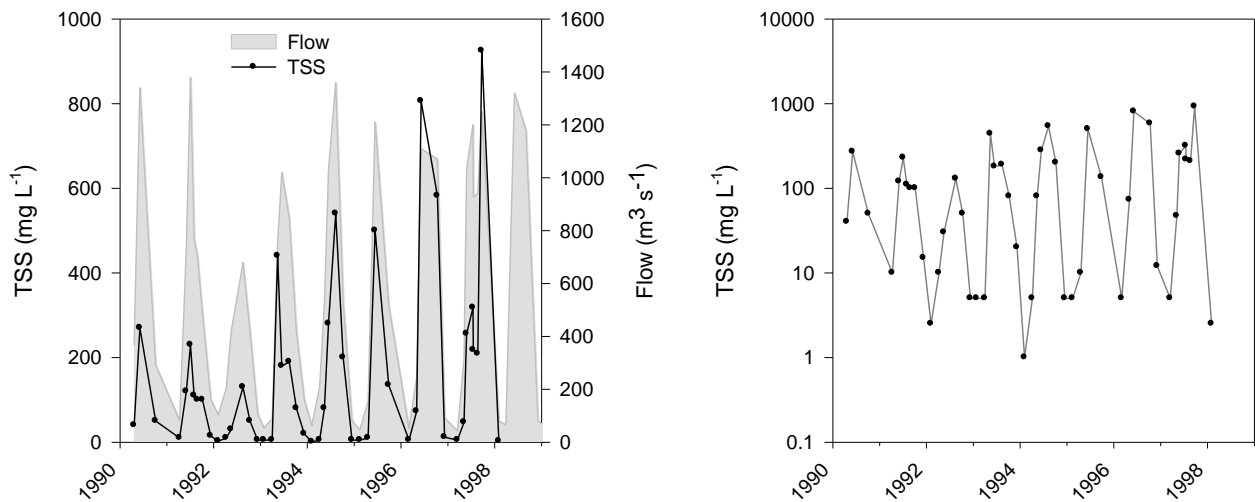
Molybdenum: Total molybdenum concentrations have been increasing in the Iskut River from 1990 to 2007 (MK test, $p < 0.05$, slope = $0.01 \mu\text{g L}^{-1} \text{a}^{-1}$; Table 1). Current molybdenum concentrations are well below the B.C. maximum aquatic life guideline of 2mg L^{-1} and the CCME aquatic life guideline of $73 \mu\text{g L}^{-1}$.

Figure 16: Total molybdenum and specific conductivity measurements (left) and log-scale total molybdenum concentrations from the Iskut River from 1990 to 2007.



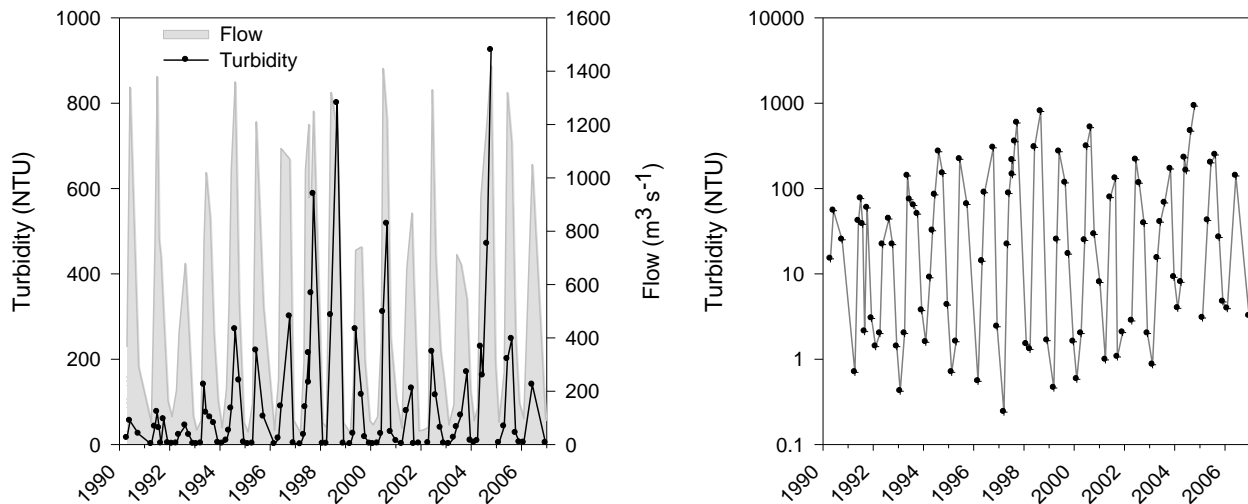
Total Suspended Solids: Total suspended solids, or TSS, was measured in the Iskut River until 1998. TSS concentrations were highly positively correlated to flow (Spearman Correlation, $r_s = 0.95$; Figure 17) and had a statistically significant increasing trend during the sample period (MK test, $p < 0.01$, slope = $4.63 \text{ mg L}^{-1} \text{ a}^{-1}$; SK test, $p < 0.05$, slope = $4.31 \text{ mg L}^{-1} \text{ a}^{-1}$; Table 1). Current B.C. water quality guidelines are dependent on background or upstream comparisons, and therefore, no guidelines comparisons can be made. A variety of total metal and nutrient concentrations are highly related to TSS and significant increases in TSS can result in corresponding trends in total metal concentrations.

Figure 17: Total suspended solids (TSS) concentrations and mean daily flow (left) and TSS concentrations in the Iskut River from 1990 to 1999.



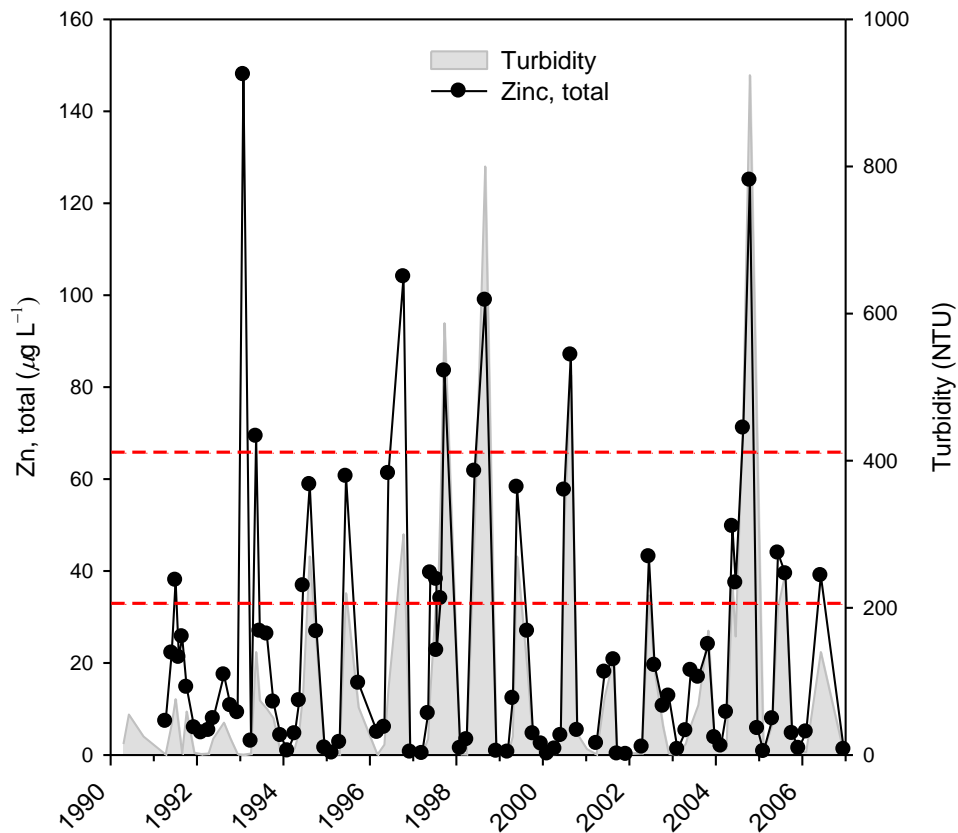
Turbidity: Turbidity measurements have increased by a statistically significant amount over the sample period in the Iskut River (MK test, $p < 0.01$, slope = 1.14 NTU a⁻¹; SK test, $p < 0.05$, slope = 1.07 NTU a⁻¹; Table 1). Similar to TSS, turbidity is strongly correlated to flow (Spearman Correlation, $r_s = 0.91$; Figure 18). Also similar to TSS, turbidity is strongly related to total metal and nutrient concentrations, and similar trends in turbidity-related parameters may result (i.e. Manganese). Turbidity guidelines are derived in a similar manner to those of TSS, and since there is no upstream, we cannot compare turbidity guidelines to B.C. guidelines.

Figure 18: Turbidity and mean daily flow measurements (left) and log-scale turbidity measurements (right) from the Iskut River from 1990 to 2007.



Zinc: Total zinc concentrations vary seasonally and are positively related to turbidity measurements (Spearman Correlation, $r_s = 0.80$; Figure 19). The current B.C. aquatic life guideline for total zinc is a hardness-dependent equation and varied from 33 to 66 $\mu\text{g L}^{-1}$ over the sample period; the CCME aquatic life guideline is 30 $\mu\text{g L}^{-1}$. Turbidity-driven spikes exceeded these calculated thresholds seasonally; however, since total zinc is strongly correlated with turbidity, these elevated concentrations are likely bound to particulate matter and not bioavailable.

Figure 19: Total zinc and turbidity measurements from the Iskut River from 1990 to 2007.



Note: Dashed red lines denotes minimum and maximum total zinc thresholds calculated over the sample period.

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