

CANADA-BRITISH COLUMBIA WATER QUALITY MONITORING AGREEMENT

WATER QUALITY ASSESSMENT OF THE SALMON RIVER NEAR HYDER, ALASKA (1990 – 2007)



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EXECUTIVE SUMMARY

This report assesses eighteen years of water quality data from the Salmon River near Hyder, Alaska. The Salmon River is a trans-boundary river which flows in a southerly direction from the north central coast of the province, emptying into the north end of the Portland Canal near Hyder, Alaska (USA). The Portland Canal separates the southern portion of the state of Alaska and the north central B.C. coast (Figure 1). Environment Canada has monitored the Salmon River since 1982, collecting approximately 26 samples per year. Environment Canada and the B.C. Ministry of Environment also monitor the nearby Bear River at Stewart, B.C.

Data that had quality assurance checks performed (i.e., known errors were removed) were compared primarily to the B.C. Environment's *Approved and Working Guidelines for Water Quality*, and secondarily to the *Canadian Council of Ministers of the Environment Guidelines for the Protection of Aquatic Life Guidelines*. Of special interest were water quality levels and trends that are deemed deleterious to sensitive water uses, and specifically, to aquatic life.

CONCLUSIONS

- The water quality of the Salmon River near Hyder, Alaska, over the 1990 up to 2007 sampling period is believed to be largely influenced by natural phenomena such as glacial erosion and mineralization. Freshet events resulted in numerous exceedences in sediment-related water quality parameters, but are not deemed to be a threat to the local aquatic biota. The watershed is sparsely populated and relatively un-impacted by humans except for limited current and historical mining operations.
- The following parameters had statistically significant increasing trends: alkalinity, sodium, magnesium and turbidity.
- Many parameters had statistically significant decreasing trends: aluminum, arsenic, cadmium, chromium, cobalt, cyanide, iron, lithium, sulphate.

- Arsenic, cadmium, chromium, colour, copper, iron, lead and zinc seasonally exceed B.C. or CCME guidelines; the values that exceeded guidelines are largely related to particulate matter (turbidity) during freshet events and unlikely to be bioavailable.
- Total aluminum concentrations exceeded the guidelines that are expressed as dissolved concentrations of the metal.
- A number of metals need to be measured differently if comparisons are to be made to guideline values as they exist. The metals and forms required to be measured are aluminum (dissolved and inorganic monomeric when available), chromium (trivalent and hexavalent), and iron (total and dissolved).
- Cyanide needs to be measured as weak-acid dissociable and as strong-acid dissociable so that comparisons can be made to existing guideline values.
- The increased turbidity during freshet would make it necessary to treat the water to remove turbidity prior to use as a drinking water supply.

RECOMMENDATIONS

We recommend the continued monitoring of water quality at the Salmon River near Hyder, Alaska, since it is used to determine trans-boundary effects between British Columbia and Alaska, and assess the environmental impacts of upstream activities such as mining. We also recommend the installation and maintenance of a hydrometric station to assess flow as it has a major influence on water quality in the Salmon River and to assess changing melting patterns over time due to factors such as climate change. Finally, we recommend that concentrations of the following parameters be measured in the following forms: aluminum should be measured as dissolved aluminum, iron as dissolved, and chromium as Cr⁺⁶ and Cr⁺³.

ACKNOWLEDGEMENTS

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INTRODUCTION

The Salmon River near Hyder, Alaska, is located in the north central coast area of B.C. (Figure 1). The drainage area of the Salmon River near Hyder is not known, but estimated at 300 km². There is no known established hydrometric station along the Salmon River.

This long-term water quality monitoring station was established to evaluate water quality and to assess if there were any long-term water quality trends in this trans-boundary river which flows from Canada to the Portland Canal, USA (Alaska). This report assesses the 18 years of data from 1990 through 2007. Environment Canada has monitored the water quality at this station since 1982, and the data are stored on the federal data base, ENVIRODAT, under station number AK08DC0001 (latitude 56° 01' 18" by longitude 130° 04' 17"). The data is also stored in the B.C. government database, EMS (station ID E237496). A nearby water quality monitoring station is located on the Bear River in Stewart, B.C., which also empties into the Portland Canal (Figure 1).

The watershed upstream from Hyder is relatively pristine with little human habitation, but historic and current upstream mining activity has likely impacted water quality. The Summit Lake mine is currently operated by Tenajon Resources with test operations conducted as recently as 2005 (MINFILE No 104B 034). The Westmin Premier gold mine operated from 1989 to 1995, but has since been placed in long-term care (MINFILE No 104B 054).

There are three glaciers, the Texas Glacier, the Boundary Glacier and the Salmon Glacier, within this watershed which have an overarching effect on water quality, and in particular with turbidity, total metals and colour. Changes in the concentration of these parameters are a result of mineralization from the release of sediment from glacial melt.

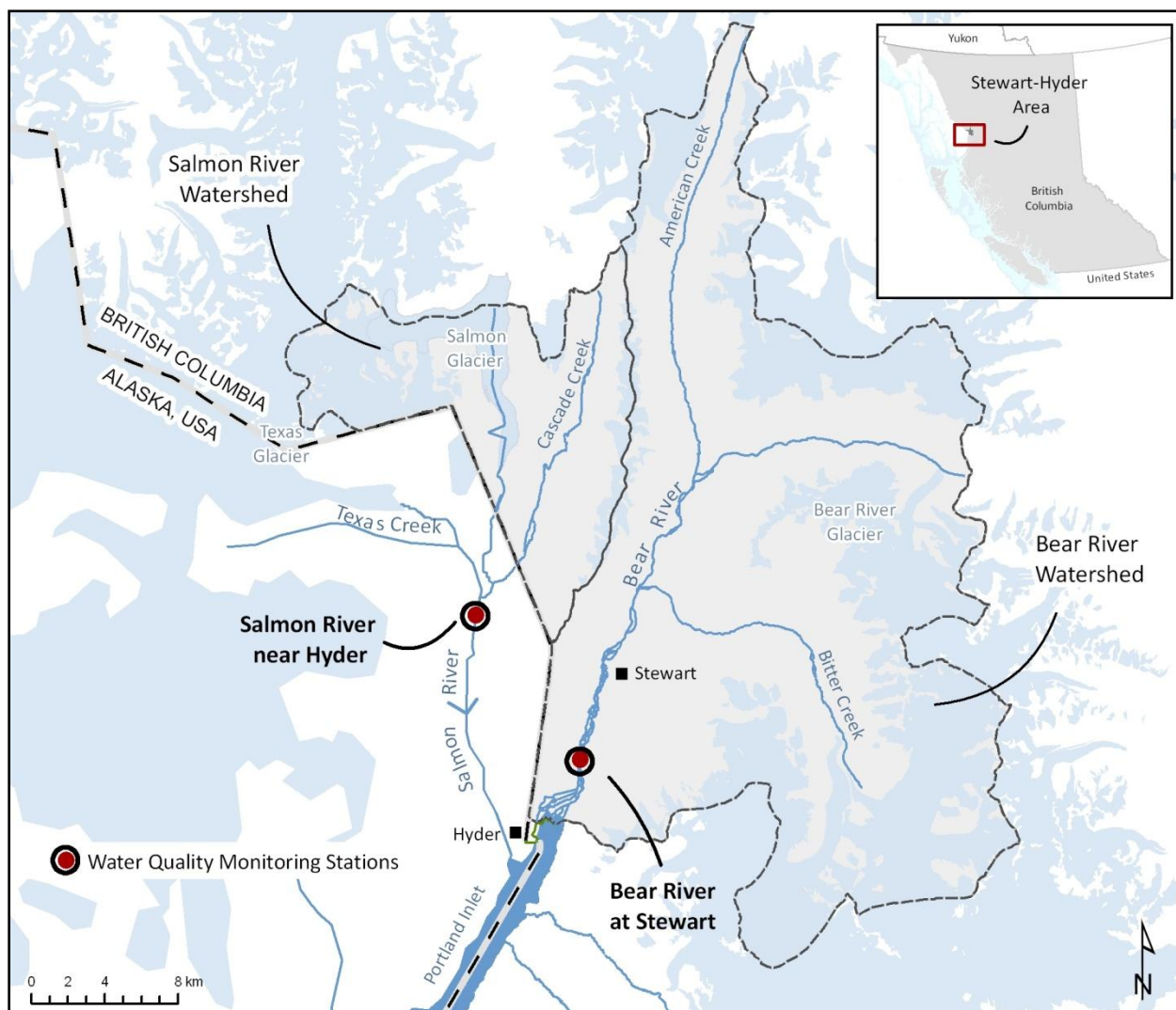


Figure 1: Map of the Salmon River.

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 is 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. Spearman Rank Correlation was used to determine parameters that can be defined by turbidity seasonality, and then the seasonality for each parameter was tested using the Kruskal-Wallis test. Parameters which had significant seasonal differences were further tested for trends using the SK trend test ($\alpha < 0.05$).

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 Guidelines 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 the Salmon River. Substances not discussed below met or rarely exceeded guidelines and displayed no significant trends and include the following: ammonia, antimony, barium, beryllium, bismuth, boron, bromide, dissolved calcium, specific conductivity, hardness, manganese, nickel, nitrogen and its constituents, phosphorus,

potassium, total dissolved solids (TDS), total suspended solids (TSS), selenium, silicon, silica, silver, strontium, water temperature, thallium, tin, 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 (MK) Test		Seasonal Kendall (SK) Test	
	P-value	Slope (units a ⁻¹)	P-value	Slope (units a ⁻¹)
Alkalinity (mg L ⁻¹)	ns	na	<0.01	0.143
Aluminum, total (µg L ⁻¹)	ns	na	<0.01	-3.167
Arsenic, total (µg L ⁻¹)	<0.05	-0.011	<0.01	-0.016
Cadmium, total (µg L ⁻¹)*	<0.01	0.000	<0.01	-0.001
Chromium, total (µg L ⁻¹)*	<0.01	-0.011	<0.01	-0.013
Cobalt, total (µg L ⁻¹)*	<0.01	-0.005	<0.01	-0.007
Cyanide, total (µg L ⁻¹)	<0.01	-0.047	<0.01	-0.095
Iron, total (µg L ⁻¹)	ns	na	<0.01	-3.988
Lithium, total (µg L ⁻¹)	<0.05	-0.008	<0.01	-0.011
Magnesium, ext. (mg L ⁻¹)	<0.01	0.025	na	na
pH (units)	<0.01	-0.012	na	na
Sodium, ext. (mg L ⁻¹)	<0.01	-0.031	<0.01	0.033
Sulphate, dissolved (mg L ⁻¹)	<0.01	-0.709	<0.01	-2.29
Turbidity (NTU)	<0.01	0.055	<0.01	0.030

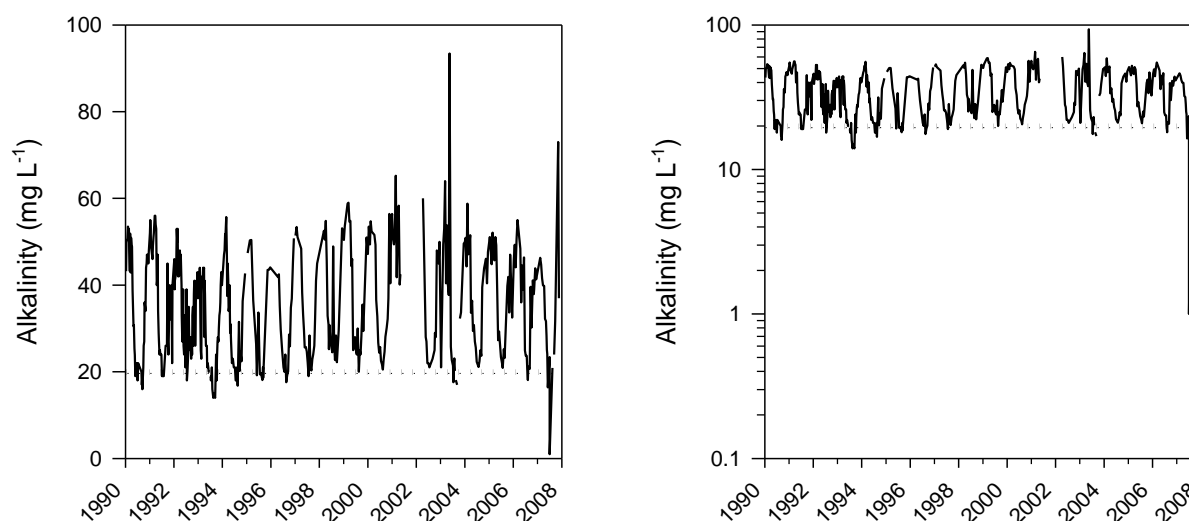
*Decrease likely due to changing minimum detection limits (MDLs)

ns, non-significant

na, not applicable

Alkalinity: Alkalinity refers to the acid neutralizing capacity of a water system as measured by the total quantity of base present. Alkalinity (as CaCO_3) levels vary seasonally with lower values near or less than 20 mg L^{-1} – the upper threshold for systems which are moderately sensitivity to acid inputs as outlined in the B.C. Working Water Quality Guidelines – during the summer season (Figure 2) when flows are suspected to be high due to snowmelt. Higher values of alkalinity would likely occur at low flow when the influence of groundwater contributions on the base flow would be greatest. Typical concentrations suggest that this system is not sensitive to acid inputs. MK trend analysis resulted in no significant trend ($p = 0.41$); however, SK trend analysis resulted in a significant increasing trend (Table 1) in alkalinity ($p < 0.01$; slope = $0.143 \text{ mg L}^{-1} \text{ year}^{-1}$).

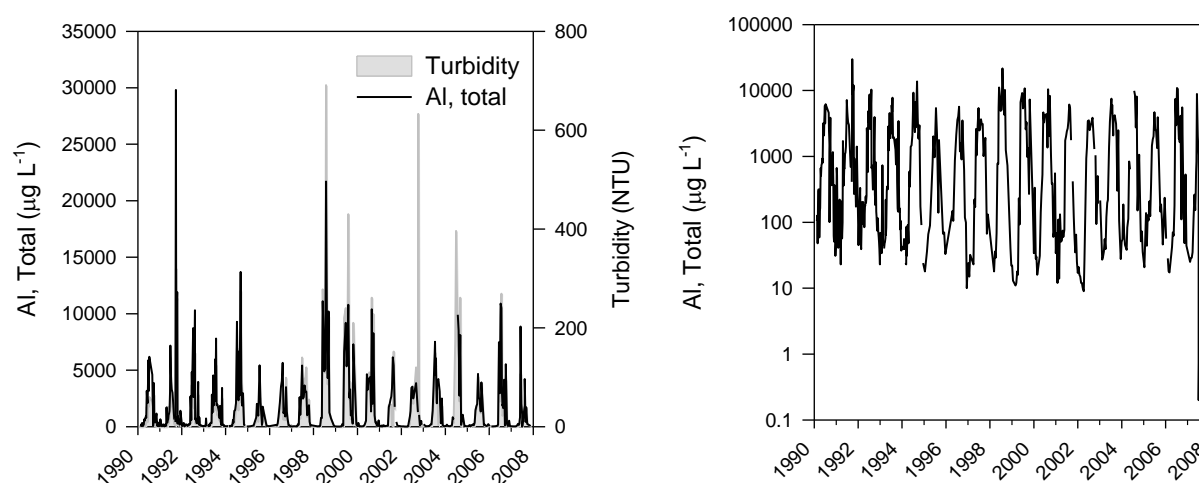
Figure 2: Total alkalinity normal- (left) and log-scale (right) concentrations from 1990 to 2008.



Note: dotted line represents the upper threshold for moderately acid-sensitive systems.

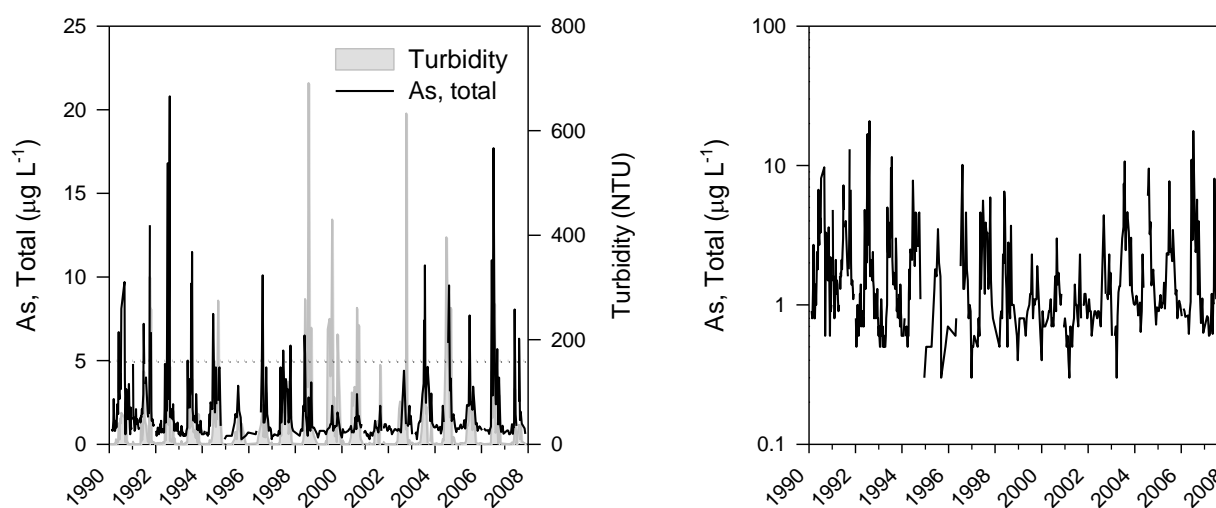
Aluminum: Total aluminum varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.91$; Figure 3) which suggests that spikes are related to suspended sediment. MK trend analysis resulted in no significant trend; however, SK analysis results indicate a statistically significant decreasing trend in total aluminum since 1990 ($p < 0.01$; slope = $-3.167 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1). The current B.C. guideline to protect aquatic life is set for dissolved aluminum at $100 \mu\text{g L}^{-1}$. Although not strictly comparable, total aluminum concentrations often exceed the water quality guideline for aquatic life. However, these seasonal spikes are highly correlated with turbidity and thus, likely bound with particulate matter and not biologically available. Efforts should be made to measure the dissolved form of aluminum. As well, CCME (2005 draft) are considering revising the guideline to protect aquatic life to the inorganic monomeric form. If this happens, this form should be measured as well; however, at present, few laboratories have the capability to measure this form.

Figure 3: Total aluminum and turbidity (left) and total aluminum (log-scale) concentrations from 1990 to 2008.



Arsenic: Total arsenic concentrations are strongly correlated with turbidity (Spearman Correlation, $r_s = 0.68$; Figure 4) which suggest that spikes in total arsenic concentrations are largely a function of suspended sediment concentration. MK and SK trend analyses resulted in significant decreasing trends (MK, $p < 0.05$, slope = $-0.011 \mu\text{g L}^{-1} \text{ year}^{-1}$; SK, $p < 0.01$, slope = $-0.016 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1). Seasonal turbidity-associated spikes in total arsenic tended to exceed the B.C. water quality guideline for aquatic life of $5 \mu\text{g L}^{-1}$ (Figure 4). Total arsenic concentrations periodically exceed the B.C. water quality guideline for aquatic life ($5 \mu\text{g L}^{-1}$). However, these seasonal spikes are highly correlated with turbidity and thus, likely bound with particulate matter and not biologically available.

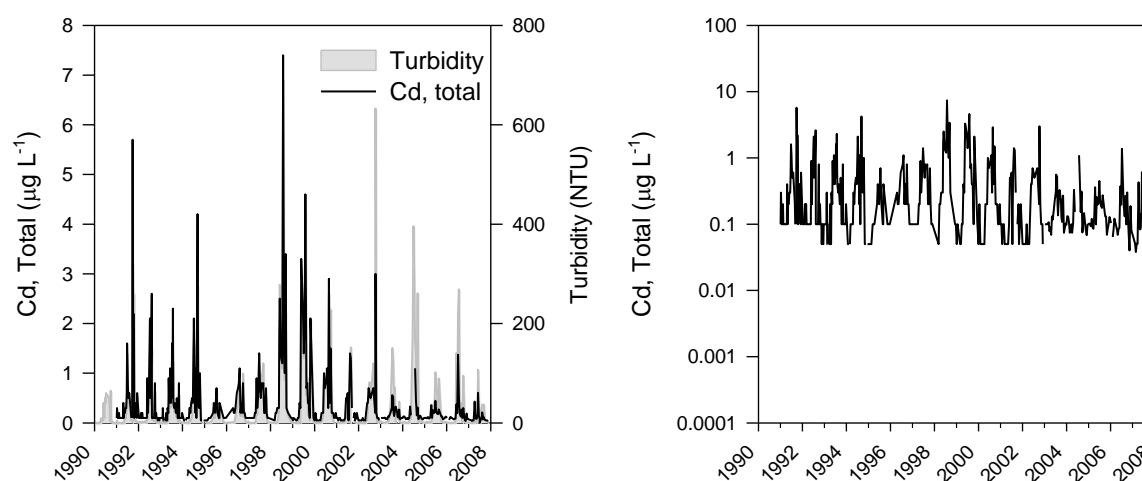
Figure 4: Total arsenic and turbidity (left) and total arsenic (log-scale) concentrations from 1990 to 2008. Dotted line represents the B.C. water quality criterion for aquatic life.



Note: The dotted line represents the B.C. Aquatic Life Water Quality Criterion for arsenic.

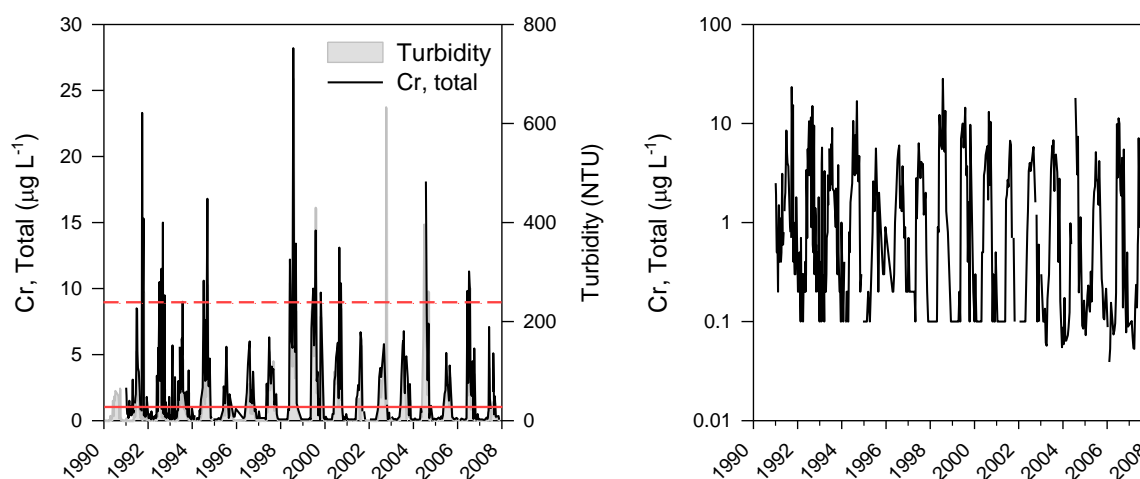
Cadmium: Total cadmium varies greatly seasonally and is strongly correlated with turbidity (Spearman Correlation, $r_s = 0.79$; Figure 5) suggesting that the spikes are related to particulate matter. Both MK and SK tests resulted in significant negative trends (MK, $p < 0.01$; SK, $p < 0.01$, slope = -0.001; Table 1). However, lowering laboratory detection limits over time have likely interfered with the statistical analyses (see Figure 5, 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 below detection limits and therefore, it is difficult to compare low-level cadmium concentrations with the guideline.

Figure 5: Total cadmium and turbidity (left) and total cadmium log-scale (right) concentrations from 1990 to 2008.



Chromium: Similar to other metals, total chromium varies greatly seasonally and is strongly correlated with turbidity (Spearman Correlation, $r_s = 0.82$, Figure 6) suggesting that spikes are related to suspended sediments. Although both MK and SK tests resulted in significant decreasing trends (MK, $p < 0.01$, slope = $-0.011 \mu\text{g L}^{-1} \text{ year}^{-1}$; SK, $p < 0.01$, slope = $-0.013 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1), changing (lowering) detection limits over time limit our ability to conclude that total chromium concentrations are decreasing (see log-scale total chromium concentrations in Figure 6). The current B.C. 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). Total chromium exceeds these guidelines seasonally, although 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.

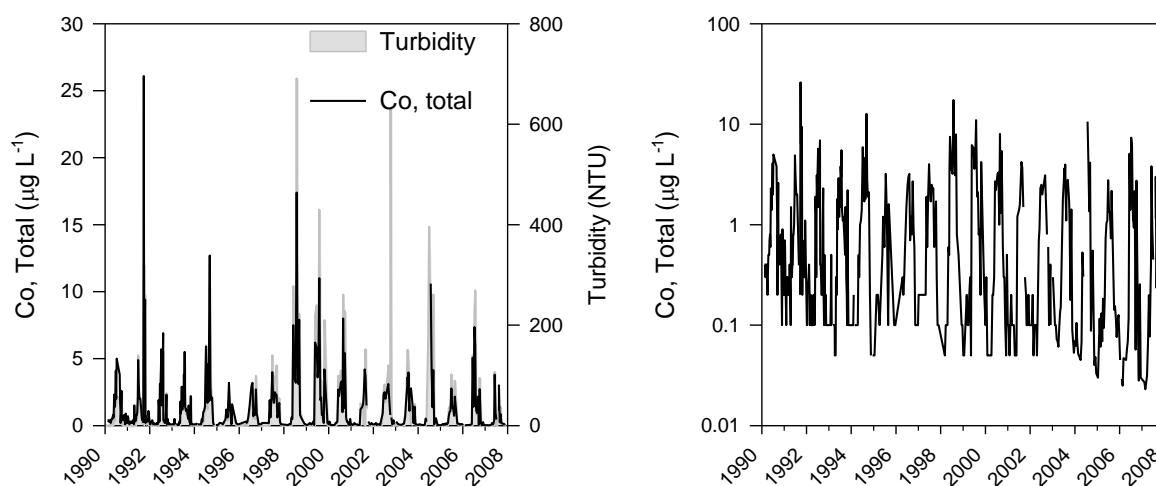
Figure 6: Total chromium and turbidity (left) and total chromium log-scale (left) concentrations from 1990 to 2008.



Note: The solid red line denotes the B.C. Working Aquatic Life Water Quality Guideline for Cr VI; the dashed-red line denotes the B.C. Working Aquatic Life guideline for Cr III.

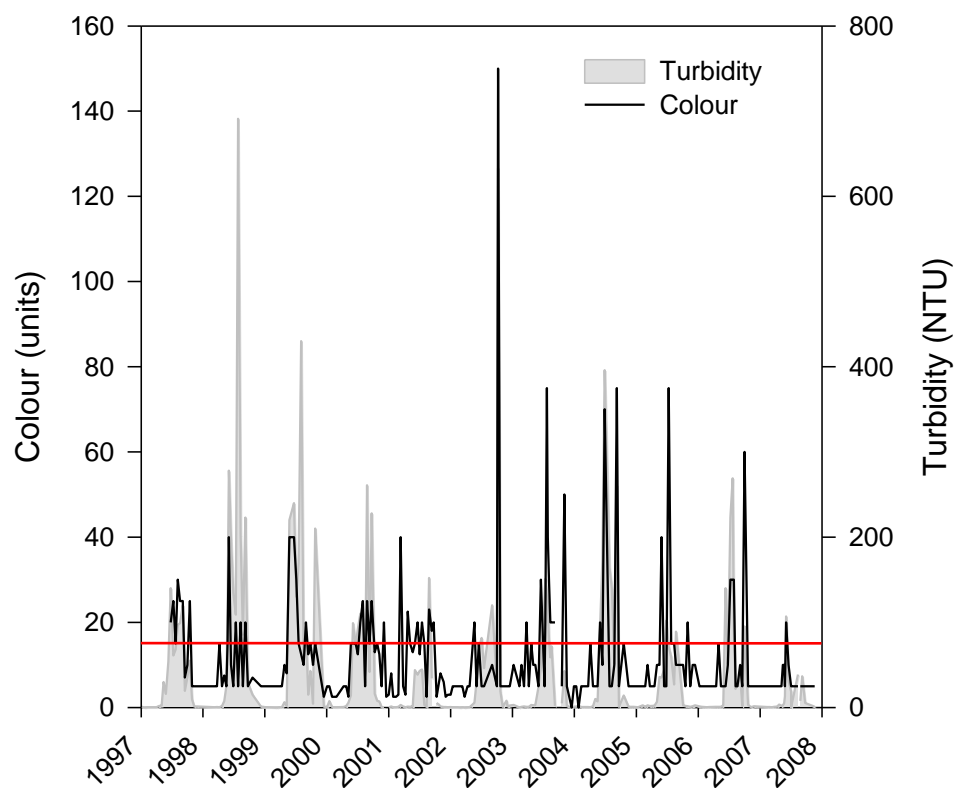
Cobalt: Similar to total cadmium and chromium concentrations, total cobalt concentrations vary seasonally and are highly correlated with turbidity (Spearman Correlation, $r_s = 0.84$; Figure 7) and thus, spikes in concentrations are unlikely to be bioavailable. Also similar to cadmium and chromium results, MK and SK statistical tests resulted in significant decreasing trends (MK, $p < 0.01$, slope = $-0.005 \mu\text{g L}^{-1} \text{ year}^{-1}$; SK, $p < 0.01$, slope = $-0.007 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1) which are likely the result of changing (lowering) detection limits over time (Figure 7). All values are well below the current B.C. water quality maximum aquatic life guideline for cobalt of $110 \mu\text{g L}^{-1}$.

Figure 7: Total cobalt and turbidity (left) and total cobalt log-scale (right) concentrations from 1990 to 2008.



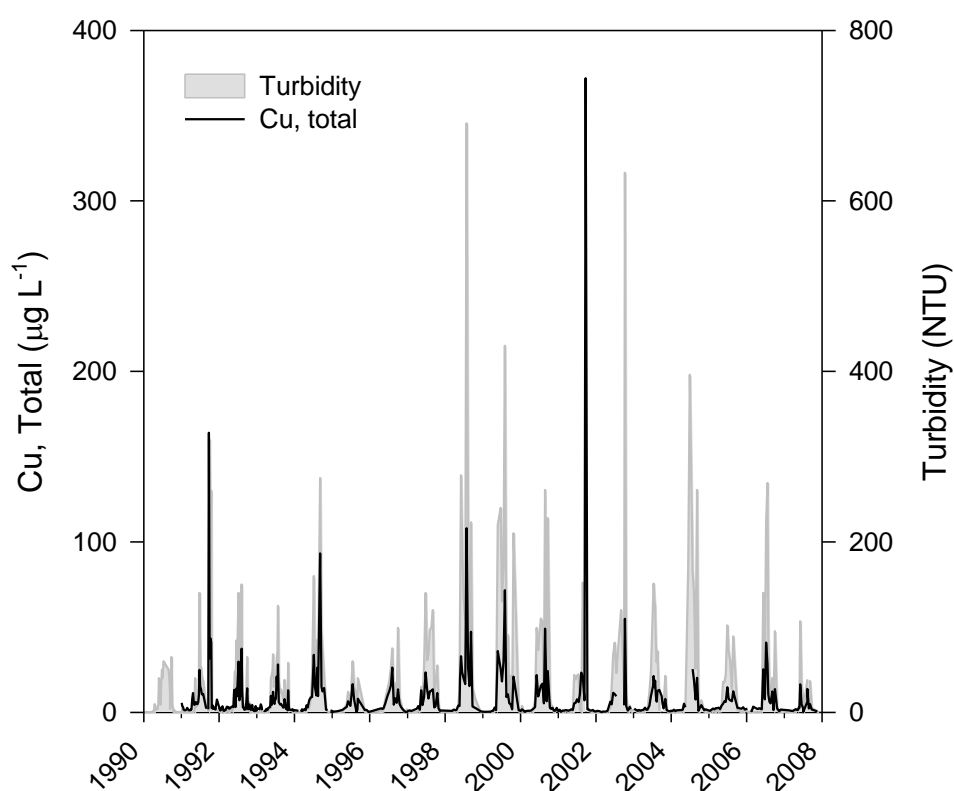
Colour: True colour has been measured from 1997 to present. Colour measurements were strongly correlated with turbidity (Spearman Correlation, $r_s = 0.63$). Colour measurements often exceed the B.C. drinking water quality guideline seasonally, but these exceedences were largely turbidity-driven (Figure 8) and not likely a result of anthropogenic inputs.

Figure 8: Colour and turbidity measurements from 1997 to 2008.



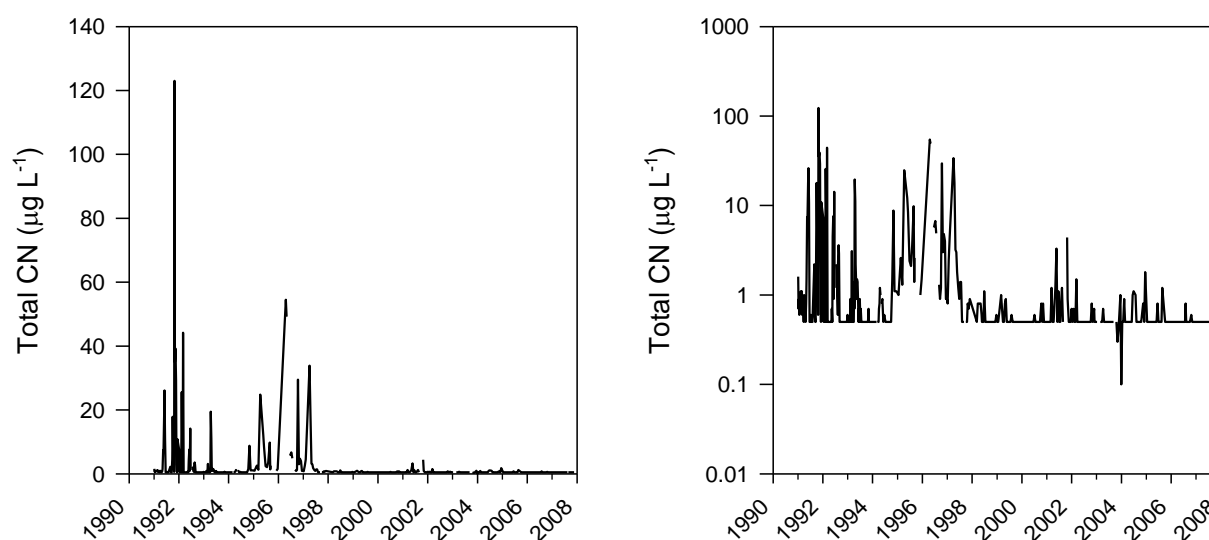
Copper: Total copper varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.87$; Figure 9) which suggests that spikes are related suspended sediment. MK trend analysis resulted in no significant trend. The BC aquatic life guideline for copper is hardness dependant and ranged from 3.5 to 12 $\mu\text{g L}^{-1}$ (median of 6.7 $\mu\text{g L}^{-1}$) during the sample period. Although baseline total copper values are at or below calculated guidelines, turbidity-associated spikes often greatly exceed these guidelines (Figure 9). However, these seasonal spikes are highly correlated with turbidity and thus, likely bound with particulate matter and not biologically available.

Figure 9: Total copper concentrations and turbidity measurements from 1990 to 2008.



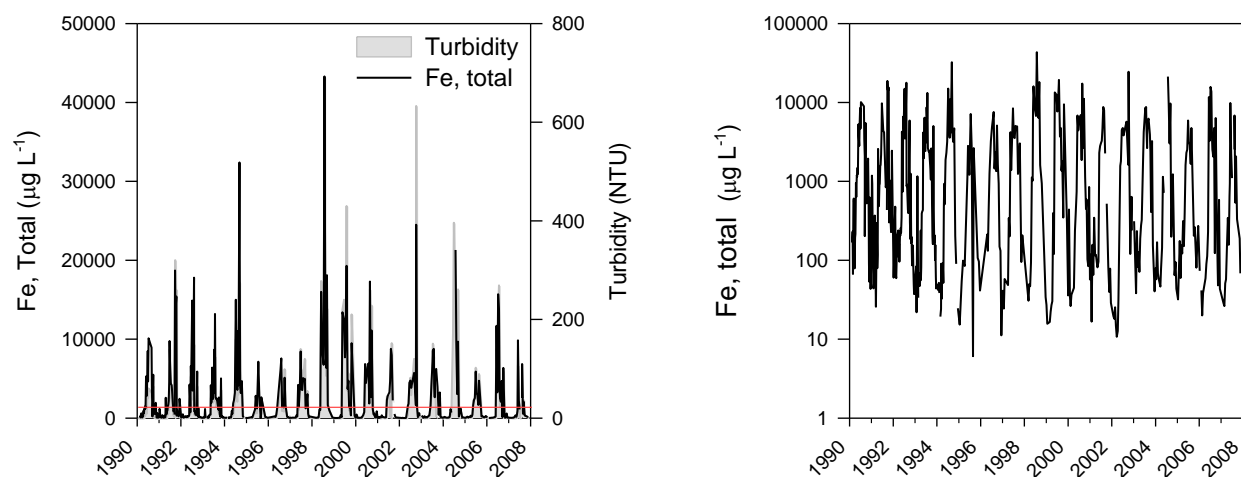
Cyanide: The B.C. guidelines for cyanide are expressed as weak-acid dissociable and strong-acid dissociable. There are no specific B.C. water quality criteria for total cyanide. Cyanide concentrations have decreased greatly from early to mid-1990 concentrations (Figure 10) which coincides with mining production. There was a significant decreasing trend for both MK trend analysis and SK analyses (MK, $p < 0.01$, slope = $-0.047 \mu\text{g L}^{-1} \text{ year}^{-1}$; SK, $p < 0.01$, slope = $-0.095 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1). Efforts should be made to measure the weak-acid dissociable and strong-acid dissociable forms of cyanide so that comparisons to guidelines are possible. This is extremely important in a gold mining area such as this where cyanide has likely been used for gold extraction through time.

Figure 10: Normal (left) and log-scale (right) total cyanide concentrations from 1990 to 2008.



Iron: Total iron concentrations vary seasonally and are strongly correlated with turbidity (Spearman Correlation, $r_s = 0.91$; Figure 11) and thus, spikes are likely related to suspended sediments. The MK test resulted in no statistical trend, however, the SK test resulted in a significant decreasing trend in total iron concentrations (SK, $p < 0.01$, slope = $-3.988 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1). Baseline total iron concentrations are well below the B.C. aquatic life water quality guideline of $1000 \mu\text{g L}^{-1}$; turbidity-driven spikes greatly exceed this criterion but are highly correlated with particulate matter and not likely bioavailable. Dissolved iron concentrations should also be measured so that comparisons to that guideline ($350 \mu\text{g/L}$) can be made.

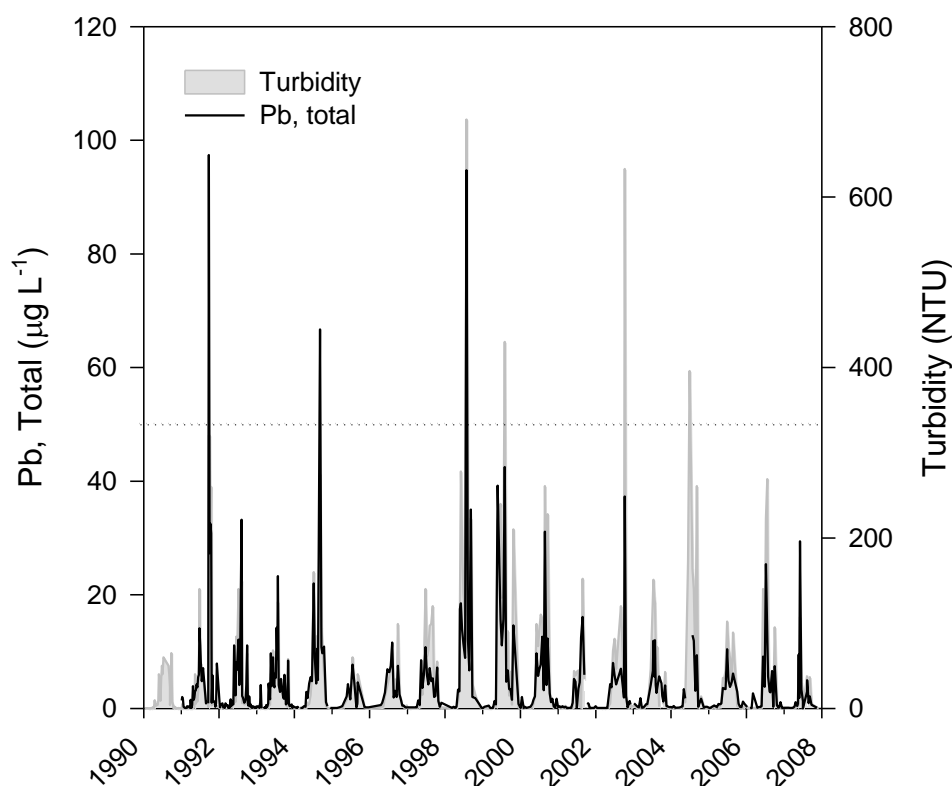
Figure 11: Normal (left) and log-scale (right) total iron concentrations from 1990 to 2008.



Note: The red line represents the B.C. Aquatic Life Water Quality Criterion of $1000 \mu\text{g L}^{-1}$.

Lead: Total lead varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.90$; Figure 12) which suggests that spikes are related suspended sediment. MK trend analysis resulted in no significant trend. The BC aquatic life guideline for total lead is hardness dependant and ranged from 8 to 89 $\mu\text{g L}^{-1}$ (median of 34 $\mu\text{g L}^{-1}$) during the sample period. Although baseline total lead values are at or below the B.C. aquatic life water quality guideline, turbidity-associated spikes often greatly exceed this guideline; total lead concentrations rarely exceed the B.C. Drinking Water Quality Criterion of 50 $\mu\text{g L}^{-1}$ (Figure 12). These seasonal spikes are highly correlated with turbidity and thus, likely bound with particulate matter and not biologically available.

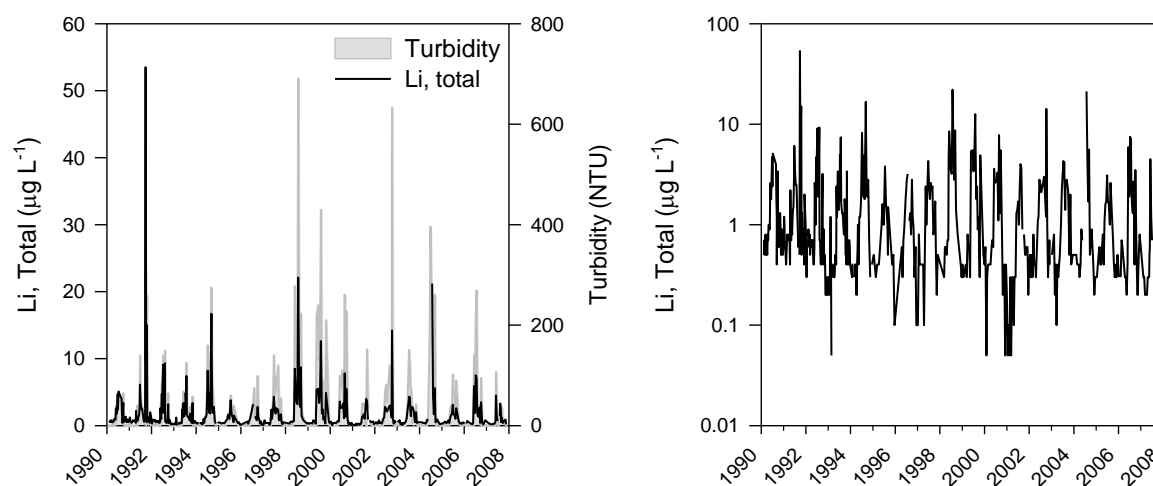
Figure 12: Total lead concentrations and turbidity measurements from 1990 to 2008.



Note: The dotted line represents the B.C. Drinking Water Quality Criterion for total lead.

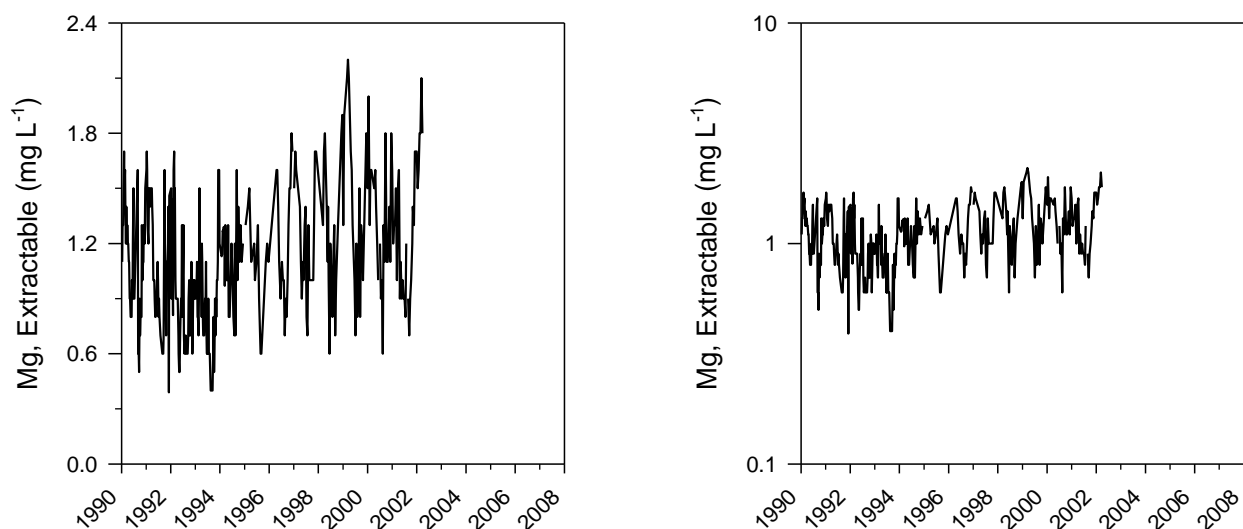
Lithium: Total lithium concentrations are strongly correlated with turbidity (Spearman Correlation, $r_s = 0.81$; Figure 13) which suggest that spikes in total lithium concentrations are largely a function of suspended sediment concentration and thus, unlikely to be bioavailable. MK and SK trend analyses resulted in significant decreasing trends (MK, $p < 0.05$, slope = $-0.008 \mu\text{g L}^{-1} \text{ year}^{-1}$; SK, $p < 0.01$, slope = $-0.011 \mu\text{g L}^{-1} \text{ year}^{-1}$; Table 1). Total lithium concentrations are well below the B.C. Working water quality guideline for aquatic life which is a maximum of $870 \mu\text{g L}^{-1}$.

Figure 13: Total lithium and turbidity (left) and total lithium log-scale (left) concentrations from 1990 to 2008.



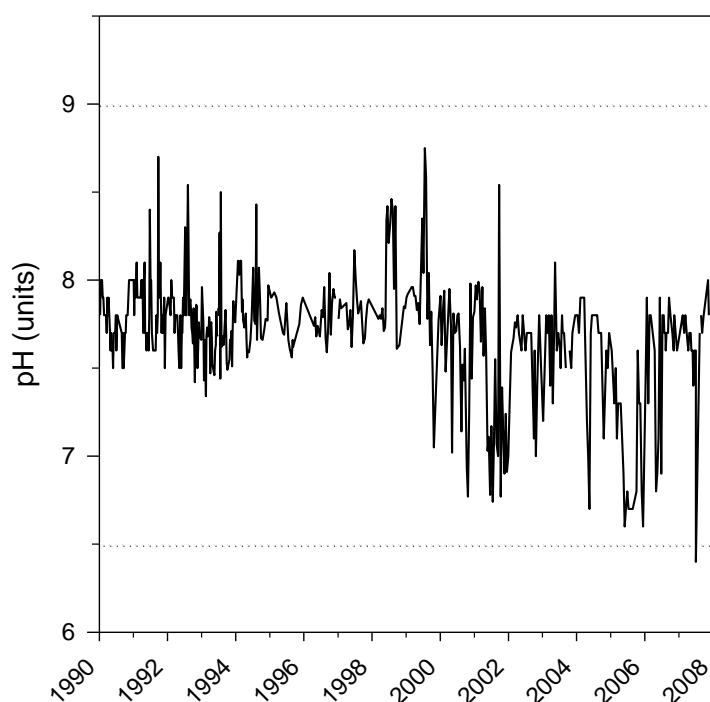
Magnesium: Extractable magnesium was analysed until 2002 and there was a significant increasing trend in the concentration of extractable magnesium during this time (MK, $p < 0.01$, slope = $0.025 \text{ mg L}^{-1} \text{ year}^{-1}$; Table 1; Figure 14). Dissolved magnesium, measured from 2002, does not appear to be increasing in concentration although statistical trends were not performed due to a limited dataset. Dissolved magnesium measurements are used to calculate total hardness in conjunction with dissolved calcium. There is no guideline for magnesium.

Figure 14: Normal (left) and log-scale (right) extractable magnesium concentrations from 1990 to 2002.



pH: There was a significant decreasing trend in pH measurements from 1990 to 2008 (MK trend test, $p < 0.01$, slope = -0.012 units year⁻¹, Table 1, Figure 15). Although pH measurements remain slightly basic and well within the B.C. water quality guideline for aquatic life of a minimum pH of 6.5 and a maximum of 9.0, recent measurements from the year 2000 onwards show depressions typically associated with late-spring and summertime samples. This change in pH patterns is taking place for one of three possible reasons: a natural change; change associated with reduced mining activity; or the fact that pH analytical methods have changed to low-ionic strength meters during the sample period and these meters provide more accurate results but may have resulted in a false trend. Typical pH measurements remain slightly basic; only one sample was slightly less than the minimum aquatic life guideline of 6.5.

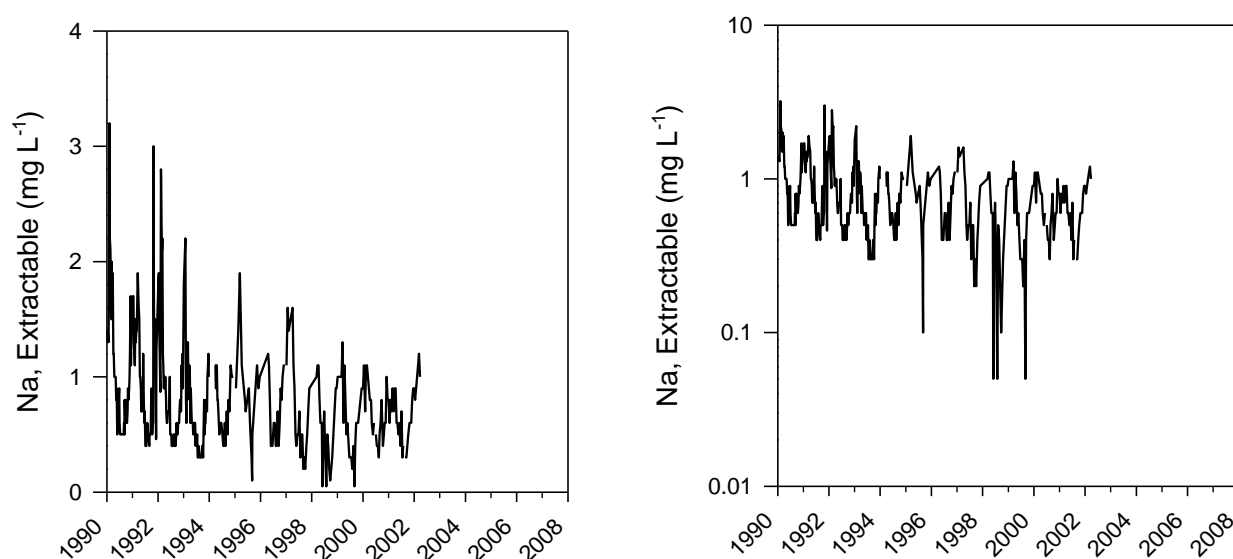
Figure 15: pH measurements from 1990 to 2008.



Dotted lines represent the B.C. aquatic life criteria for pH of a minimum of 6.5 and maximum of 9.0 pH units.

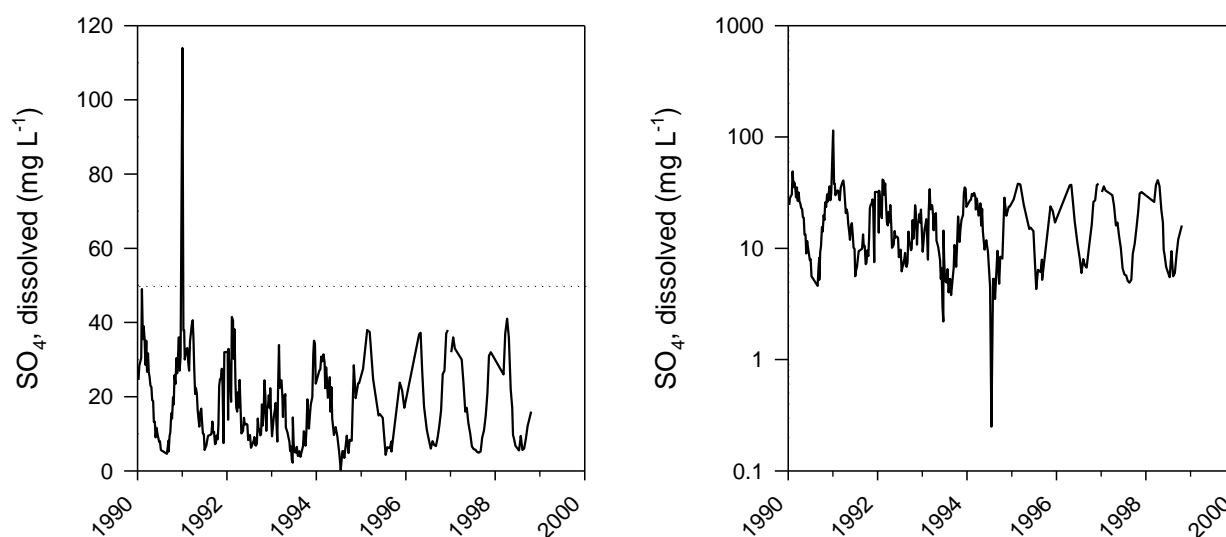
Sodium: Extractable sodium was analysed until 2002 and there was a highly significant decreasing trend in extractable sodium during this time (MK trend test, $p < 0.01$, slope = $-0.031 \text{ mg L}^{-1} \text{ year}^{-1}$; Table 1, Figure 16). There is currently no B.C. water quality aquatic life guideline for sodium.

Figure 16: Normal (left) and log-scale (right) extractable sodium concentrations from 1990 to 2002.



Sulphate: Dissolved sulphate was analysed until 1999. Results from measurements from 1990 to 1999 resulted in a significant decreasing trend in dissolved sulphate concentrations (MK trend analysis, $p < 0.01$, slope = $0.025 \text{ mg L}^{-1} \text{ year}^{-1}$; Table 1; Figure 17). Dissolved sulphate concentrations were below the B.C. criterion for aquatic life (100 mg L^{-1}). Sulphate concentrations in the river could in part be the result of acid mine drainage that may be associated with the mining operations.

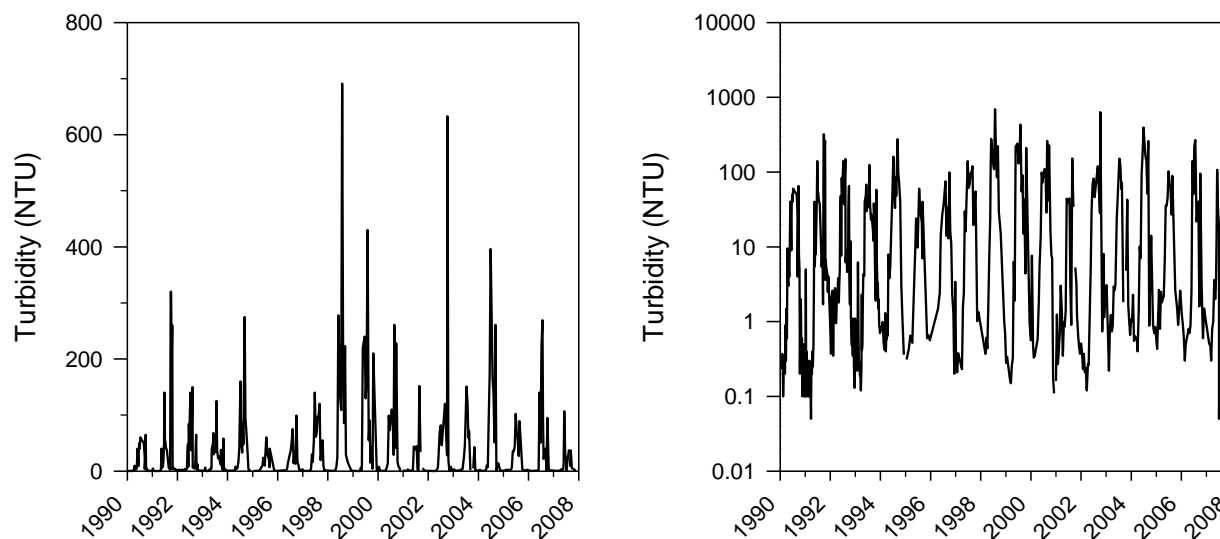
Figure 17: Normal (left) and log-scale (right) dissolved sulphate concentrations from 1990 to 1999.



Note: The dotted line represents the B.C. water quality alert level to monitor the health of aquatic mosses.

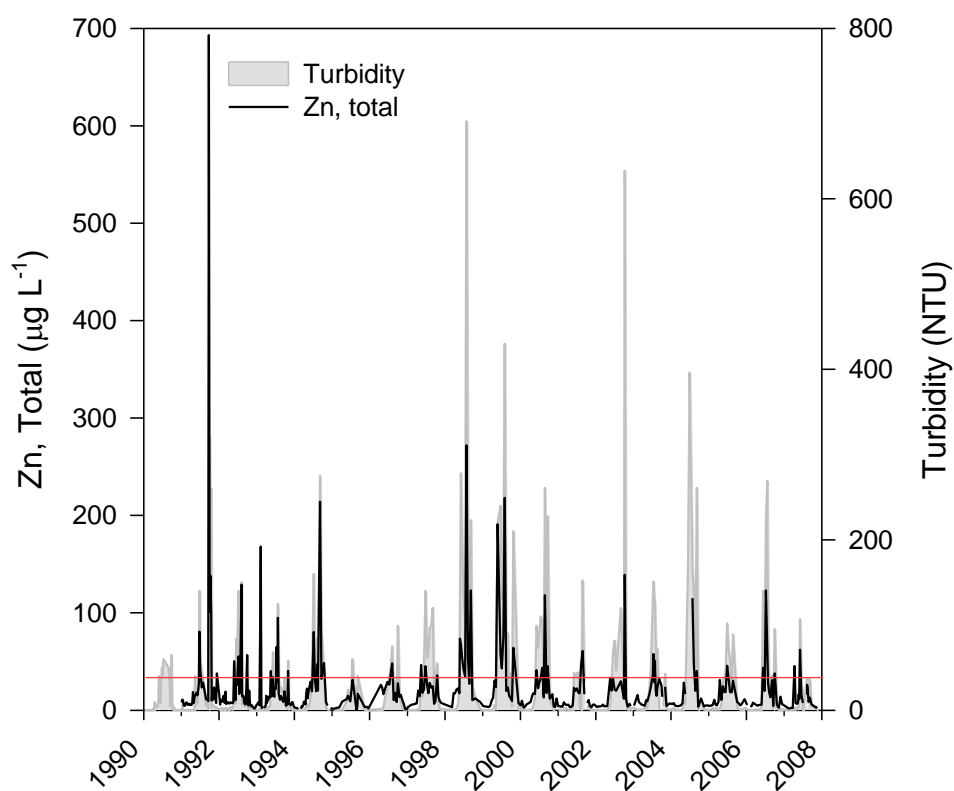
Turbidity: There has been a highly significant increase in turbidity concentrations in the Salmon River since 1990 (MK trend analysis, $p < 0.01$, slope = 0.055 NTU year⁻¹; SK trend analysis, $p < 0.01$, slope = 0.030 NTU year⁻¹; Table 1; Figure 18). Changing flow and glacial melting patterns are likely the main cause, although mining activities potentially to a lesser extent could be contributing. We cannot confirm these as the only or main factors at this time. Since metals and nutrients are often measured in their total form (i.e. with particulate or sediment-bound matter included), increases in turbidity concentrations also result in increases in total metals and nutrients; however, it is unlikely that turbidity-associated spikes in metal concentrations are biologically available.

Figure 18: Normal (left) and log-scale (right) turbidity concentrations from 1990 to 2008.



Zinc: Total zinc varies greatly seasonally and has a strong positive correlation with turbidity (Spearman Correlation, $r_s = 0.82$; Figure 19) which suggests that spikes are related suspended sediment. MK trend analysis resulted in no significant trend. Although baseline total zinc values are at or below the B.C. aquatic life water quality guideline of $33 \mu\text{g L}^{-1}$, turbidity-associated spikes exceed this guideline (Figure 19). However, since these seasonal spikes are highly correlated with turbidity, they likely are not biologically available.

Figure 19: Total zinc concentrations and turbidity measurements from 1990 to 2008.



Note: The red line denotes the B.C. Aquatic Life Water Quality Guideline for total zinc.

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