

Rapid Hydrogeochemistry: A summary of two field studies from central and southern interior British Columbia, Canada using a photometer and voltammeter to measure trace elements in water

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Introduction

In this paper we informally define 'rapid hydrogeochemistry' as the field analysis of water for trace elements within 48 hours of sample collection using portable devices and producing data that approach the reliability and detection limits available from commercial laboratories. Portable and bench-top photometers and voltammeters for the analysis of trace elements in water are commercially available, but until recently these devices have not been applied to mineral exploration. Historically they have been used for testing swimming pool water, single analyte environmental testing, and for geothermal exploration (Yehia *et al.* 2013).

Taufen (1997) and Leybourne & Cameron (2010) previously demonstrated the value of hydrogeochemistry as a mineral exploration technique. Encouraged by these examples, two Geoscience BC funded field studies were carried out in 2014 and 2016 to test the practicality and capability of photometers and voltammeters for detecting hydrogeochemical anomalies associated with mineral occurrences in the central and southern interior of British Columbia (BC), Canada. Results of these studies are reported in Yehia & Heberlein (2015), and Yehia *et al.* (2017), and are summarized in this article. In 2014, water samples were collected in August and October from streams and springs draining a porphyry Cu-Mo deposit exposed on the eastern flank of Poison Mountain. In June 2016, a regional-scale hydrogeochemical survey covering 900 km² was carried out in the glaciated and mostly till-covered area near Nazko in central BC (Fig. 1). Sampling was repeated in August and October of the same year to study seasonal variations. The Nazko survey area includes two known Cu-Au mineral occurrences: Fishpot and Bob (BC Mineral Inventory – MINFILE # – 093B 066 and 093B 054).

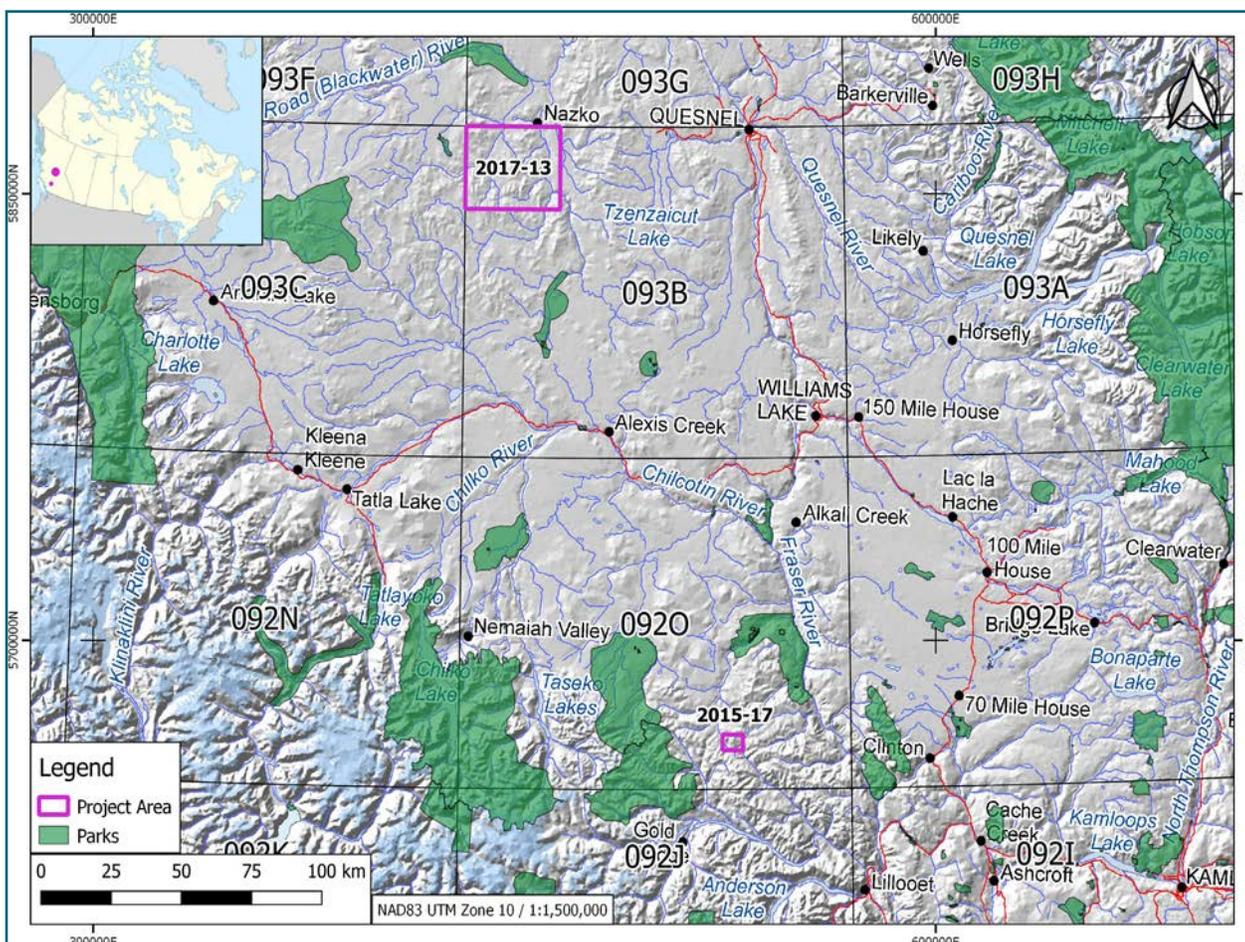


Figure 1. The location of two rapid hydrogeochemistry projects in British Columbia, Canada.

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Table 1. Summary of field and quality control samples.

Report	Field samples	Field duplicates	Analytical duplicates	Deionized water blanks	SLRS-6 standard	ALS Environmental Laboratory checks
2015-17	79	8	NA	2	NA	40
2017-13	171	9	9	10	10	23
Total	250	17	9	12	10	63

Methods

Table 1 lists the number of water and quality control samples collected during each campaign as well as samples analysed by a commercial laboratory. Samples were collected from mid-stream into #2 high-density polyethylene (HDPE) bottles and tested within 48 hours. Manufacturer's requirements state that no filtration is necessary as both devices test for dissolved constituents. As well, acidification is not required if tests are performed immediately or as soon as possible after sampling. For longer wait times needed for voltammeter tests, acidification is recommended. Samples were stored in plastic bottles in coolers. Refrigeration was not required. The primary portable analytical instrument used in both studies was the Palintest® Photometer 8000 (Fig. 2). The instrument measures the absorbance and transmittance of light through metal-colour complexes at different light wave lengths (e.g., 500 nm) to determine element concentration.

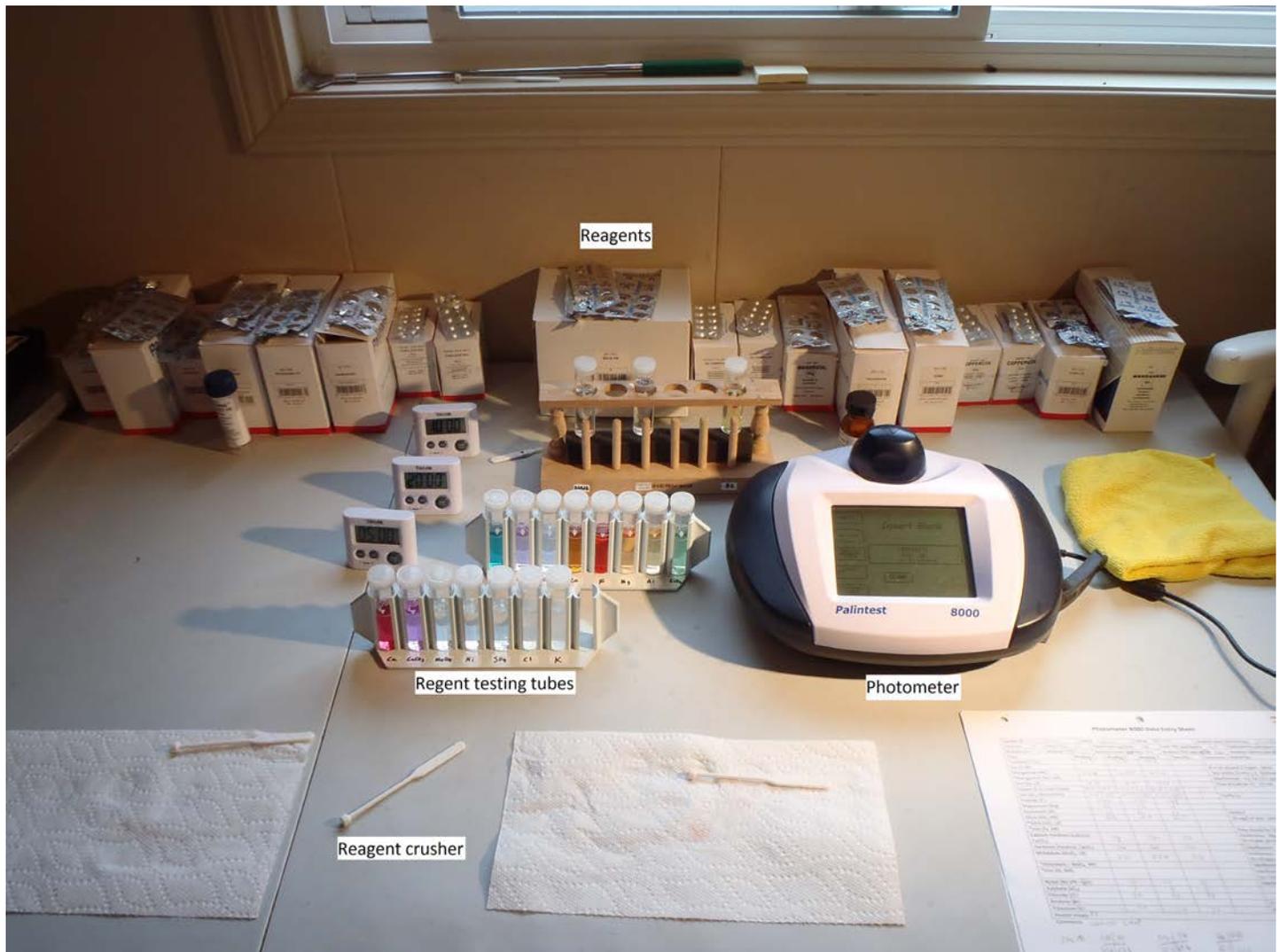


Figure 2. Photograph showing a typical set-up for 2016 photometer analysis of water samples for trace elements in a field laboratory. The reagents are in silver packages at the top of the photograph. Water samples with reagents added ready for analysis are in the 10 ml tubes held in the racks. The photometer is in the centre right.

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In addition to the photometer, the 2016 study also included the use of the Modern Water PDV6000*Ultra* voltammeter (Fig. 3). The voltammeter uses anodic stripping voltammetry (ASV) to measure the ionic concentration of metals such as Cu, As, Pb and Cd in water by applying a negative (reducing) potential for 60 seconds to the electrodes to deposit (i.e., reduce) the metal onto the electrode surface. When metal has been deposited, the metal is then stripped (oxidized) off the electrodes by increasing the potential at a constant rate. As the metal ions are released, a current is generated, which is plotted on a “voltammogram” where the analyte concentration is displayed as a function of current (voltammogram peak height on a y axis) and voltage at a specific metal oxidation potential (along the x axis). The use of field portable anode stripping voltammeters for water analysis has been described previously by Hall & Vaive (1992). Tables 2 and 3 compare the portable instrument detection limits with those of the chosen commercial laboratory.



Figure 3. Photograph from 2016 study showing the portable voltammeter set-up. The instrument is resting on top of the yellow case, and the cell containing the test electrodes and the water sample rest on a holder just above the case handle. Laptop is not required for voltammeter operation.

Table 2. Photometer reagent detection limits.

Photometer	Palintest instrument numerical detection limit (mg/l)	ALS Environmental Laboratory detection limit (mg/l)
Aluminum (Al)	0.01	0.001
Calcium hardness (Calcicol ¹)	1	1
Chloride (Cl ⁻ , Chloridol ¹)	0.1	0.5
Copper (Cu, Coppercol ² , free and total ²)	0.01	0.0002
Hardness (Hardicol ² , total)	1	1
Iron (Fe)	0.01	0.01
Magnesium (Mg)	1	0.1
Manganese (Mn)	0.001	0.0001
Molybdate (MoO ₄)	0.01	0.000050 (Mo)
Nickel (Ni)	0.01	0.0005
Potassium (K)	0.1	0.05
Silica (High Range, SiO ₂)	0.1	0.5
Sulphate (SO ₄)	1	0.3
Zinc (Zn)	0.01	0.001

¹ Calcicol, Chloridol, Coppercol and Hardicol are Palintest terminology for proprietary reagents.

² Free copper – Palintest terminology for dissolved Cu.

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Table 3. Voltammeter reagent detection limit.

Voltammeter	Modern Water published typical DL in clean water (mg/l)	ALS Environmental Laboratory detection limit (mg/l)
Arsenic (As)	0.0005	0.0001
Copper (Cu)	0.0005	0.0002
Cadmium (Cd)	0.0005	0.000005
Lead (Pb)	0.0005	0.00005

Data Quality

An important component of both studies was quality control and assessment of the dependability of the analytical results. Quality control procedures included analysis of manufacturer's standard colour solutions to monitor instrument accuracy and drift and the use of field duplicate and analytical replicate samples to monitor precision and analytical error. Three Palintest certified standard calibration solutions were measured at the beginning of each day before routine sample analysis. Calibration results demonstrated acceptable

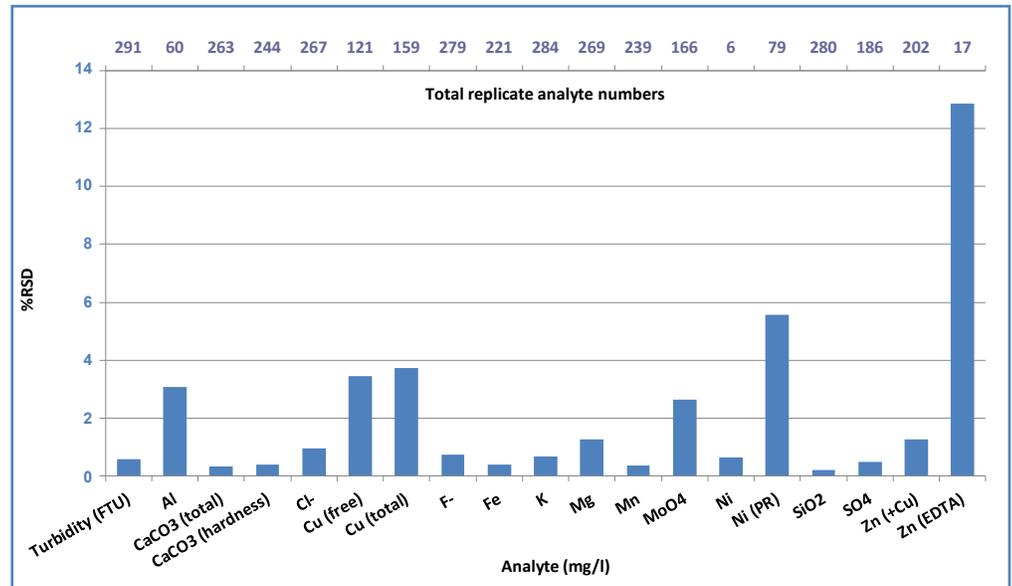


Figure 4. Percent RSD value estimates from triplicate photometer readings for the combined 2015 and 2017 results.

accuracy; no test fell outside the manufacturer's recommended margin of error of $\pm 2\%$. For the Modern Water voltammeter, accuracy was monitored using a manufacturer's calibration standard that was analyzed in triplicate before sample testing. Acceptable accuracy is defined as all three determinations falling within $\pm 5\%$ mV range.

During initial photometer testing prior to the 2014 study, it was observed that on occasion repeated photometer readings displayed small variations. Therefore, triplicate analysis of each sample was instituted as part of the standard operational procedure to quantify analytical precision (expressed as percent relative standard deviation or %RSD). Analytical precision for the two sampling campaigns are presented in Figure 4. The results show that %RSD values for most analytes are below 6%, confirming the precision of the analytical method. Zn (EDTA) has a slightly higher but still acceptable value of 13%.

Overall precision calculated from photometer field duplicate results is presented in Figure 5. The %RSD values are well within acceptable precision levels for exploration samples. The best results are for SiO₂, (5.42%), CaCO₃ (~8.0%), and Mn (6.15%) while the poorest precision was for Cl⁻ (32.03%). The photometer has larger %RSD values than the commercial laboratory because of its higher detection limits and lower display resolution.

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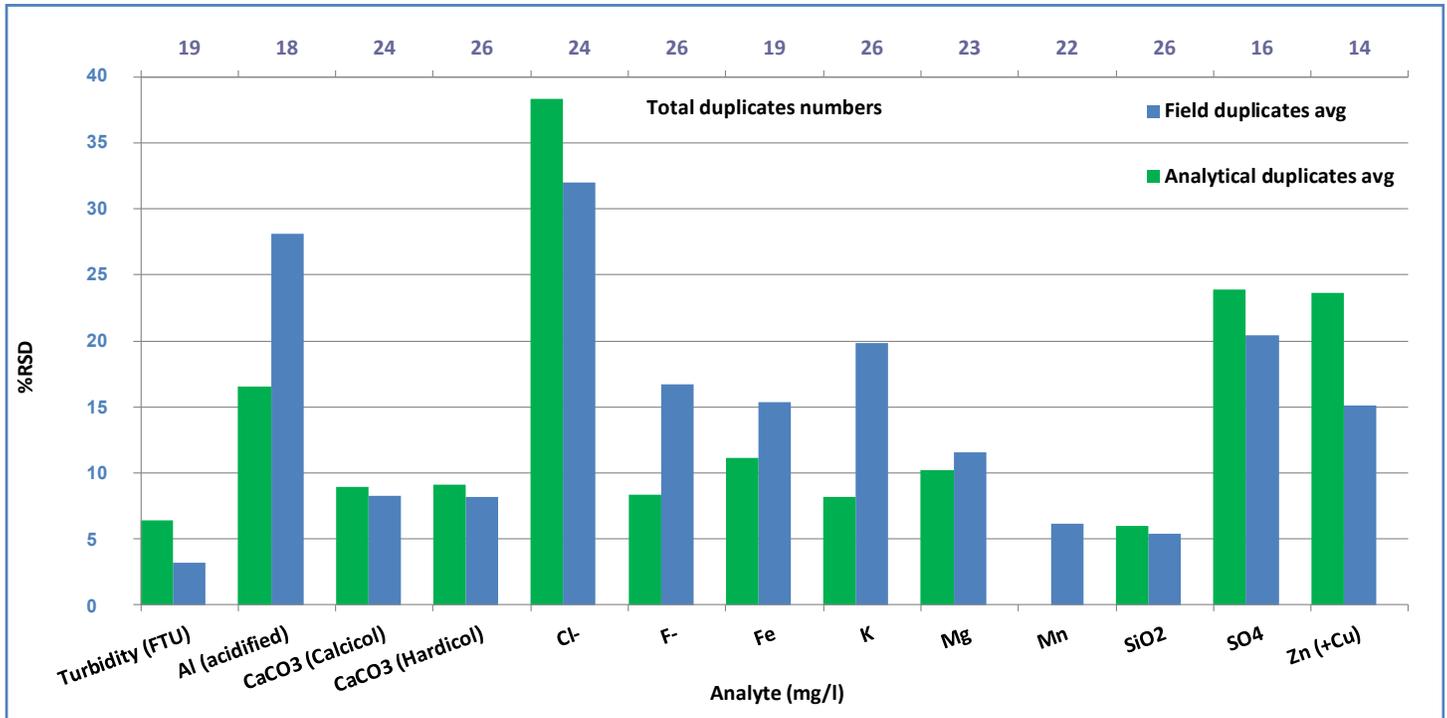


Figure 5. A summary of Photometer field and analytical precisions for the combined studies.

Only one field and analytical duplicate was measured by the voltammeter, which was insufficient to determine the %RSD. Voltammeter precision estimated from replicate analysis produced %RSD values of 9.00% for As (6 repeat analyses), 9.94% for Cu (15 repeat analyses), and 3.82% for Pb (2 repeat analyses), which are reasonable for duplicates. As part of the 2016 quality control procedures, Natural Research Council (NRC) Canada river water certified reference material (SLRS-6) was used to monitor accuracy (bias) and drift. Results are shown in Table 4 below.

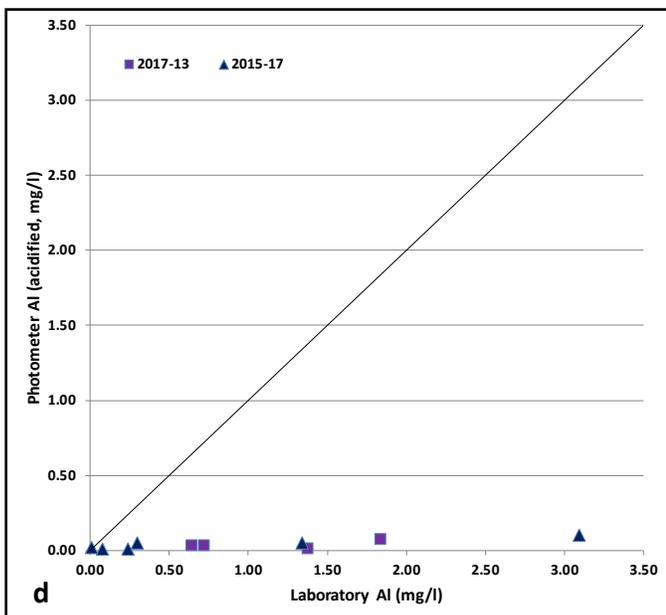
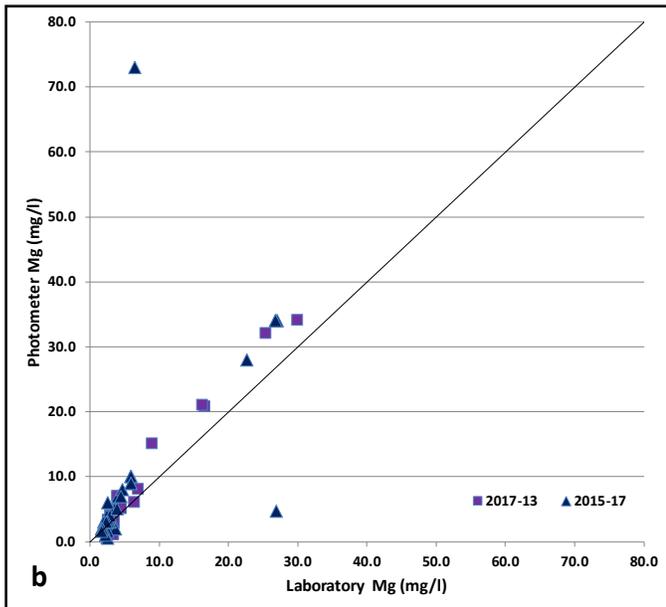
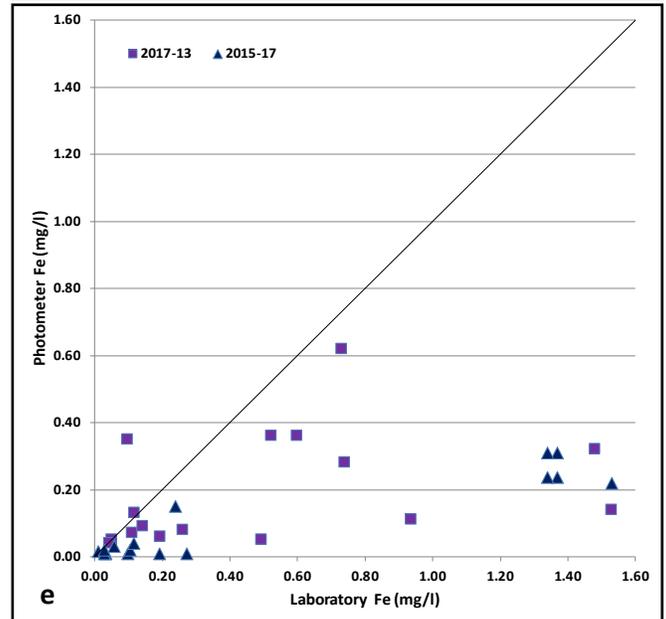
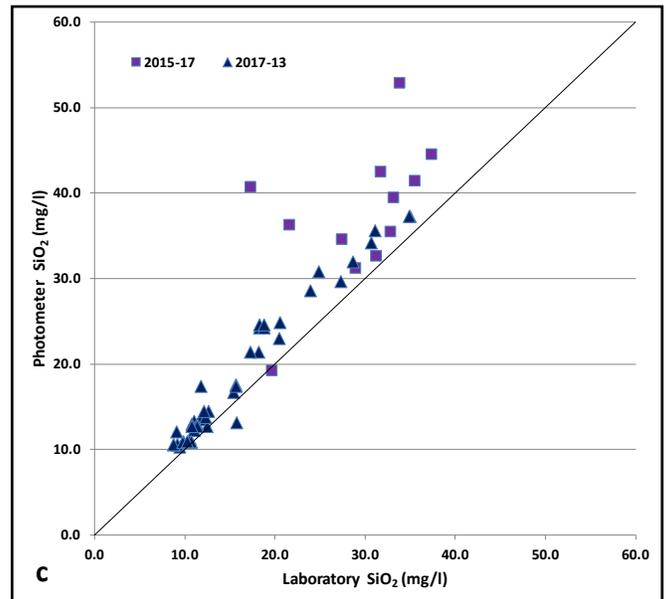
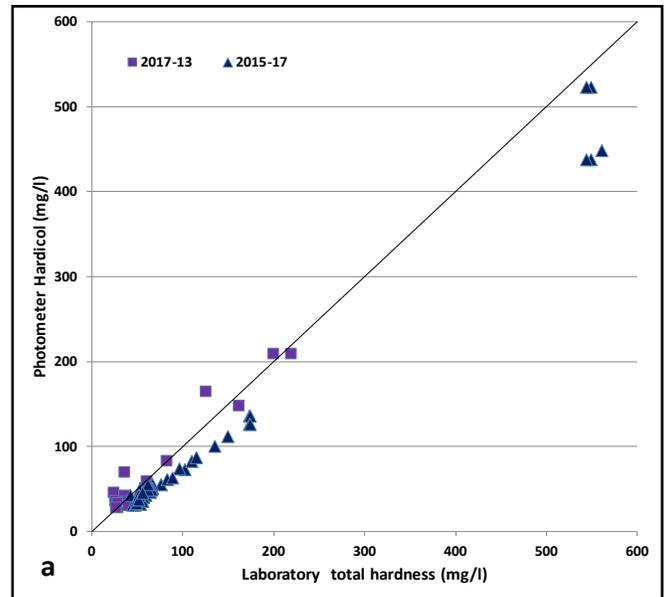
Table 4. Nazko study National Research Council Canada Natural Water Standard Concentration (SLRS-6) comparison results.

Sample ID	Photometer Al (Acidified, mg/l)	Photometer Mg (mg/l)	Voltammeter Cu (µg/l)
L160600000022	0.02	1.6	NA
L160600000054	0.03	1	23.62
L160600000079	0.03	1	19.73
L160800000083	0.03	1.3	28.01
L160800000104	0.02	3	26.47
L160800000136	0.02	4	30.51
L161000000145	0.03	3	30.05
L161000000163	0.03	2	25.72
L161000000198	0.02	4	30.59
Mean	0.026	2.322	26.838
SD	0.005	1.21	3.808
%RSD	20.62%	52.11%	14.19%
%Bias	-23.08%	8.86%	12.30%
NRC SLRS-6	0.0338	2.133	23.9

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Results produced by both instruments were compared with ALS Environmental Laboratory's ICP-OES analyses. Correlations between the photometer and laboratory data are shown for CaCO₃ Hardicol (total hardness), Mg and SiO₂ results (Fig. 6a-c). Results for these analytes in the 2014 samples display the best overall correlation. Despite showing a slight high bias in the photometer results, SiO₂ results for the 2016 samples appear to show a reasonable correlation between the laboratory and field methods. Extreme differences are apparent for Al and Fe shown in Figure 6 (d-e). These differences are attributed to the type of test the reagents perform. Whereas laboratory ICP-MS analysis provides concentrations of the cations regardless of their speciation, the photometer reagent will only interact with a specific dissolved ionic species in the test solution (Palintest personal communication). These differences are small enough for the results to still be meaningful.

Figure 6. A comparison of photometer and laboratory results for (a) Hardicol (Palintest reagent terminology for total hardness), (b) Mg, (c) SiO₂, (d) Al, and (e) Fe.



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Results

This article discusses the Poison Mountain (2014) and Nazko (2016) water sampling results for As, Cu and SO₄ for the month of October. A more comprehensive description and discussion of the results is reported by Yehia & Heberlein (2015) and Yehia et al. (2017). For the Poison Mountain study, total Cu results (Fig. 7) show elevated Cu values up to 1.60 mg/l over the mineralized zone. The highest concentrations occur in two springs (red dots; Fig. 7) in the upper reaches of 'Copper Creek' with concentrations diminishing downstream. Sulphate concentrations up to 290 mg/l (Fig. 8) in both spring and stream waters reflect drainage from the sulphide mineralized zone. Elevated concentrations persist downstream for about four kilometres as a strong dispersion trend along Poisonmount Creek.

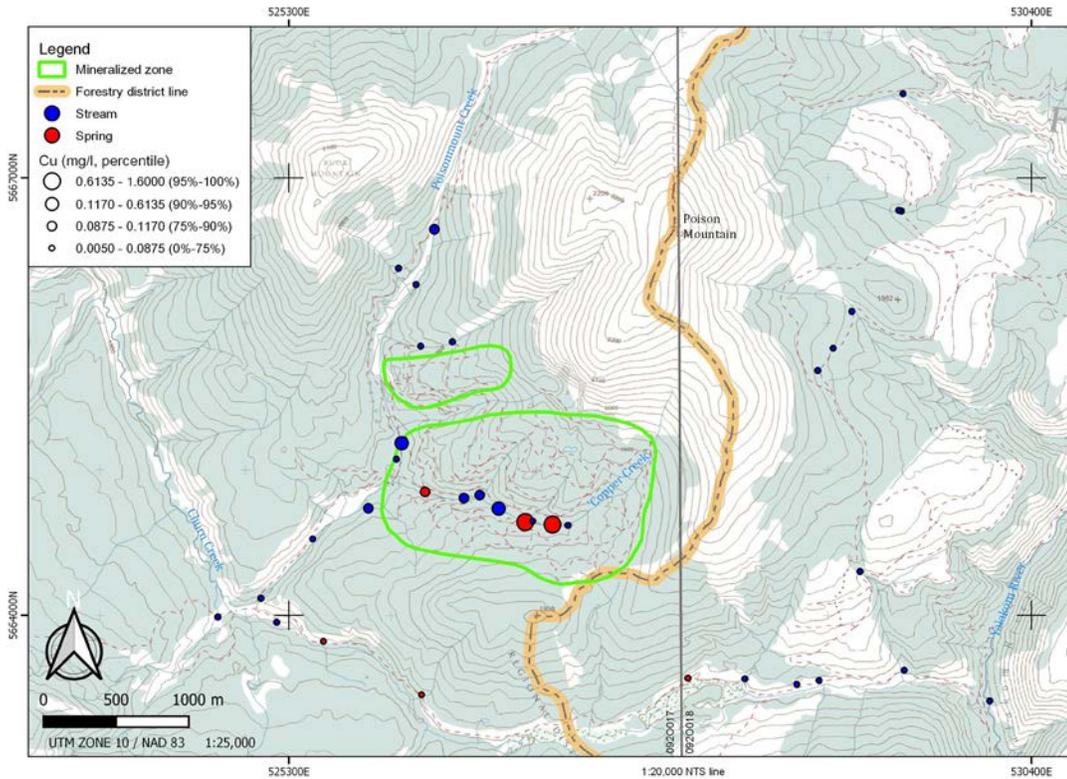


Figure 7. Report 2015-17 October photometer Cu (total) results for water samples from the Poison Mountain study.

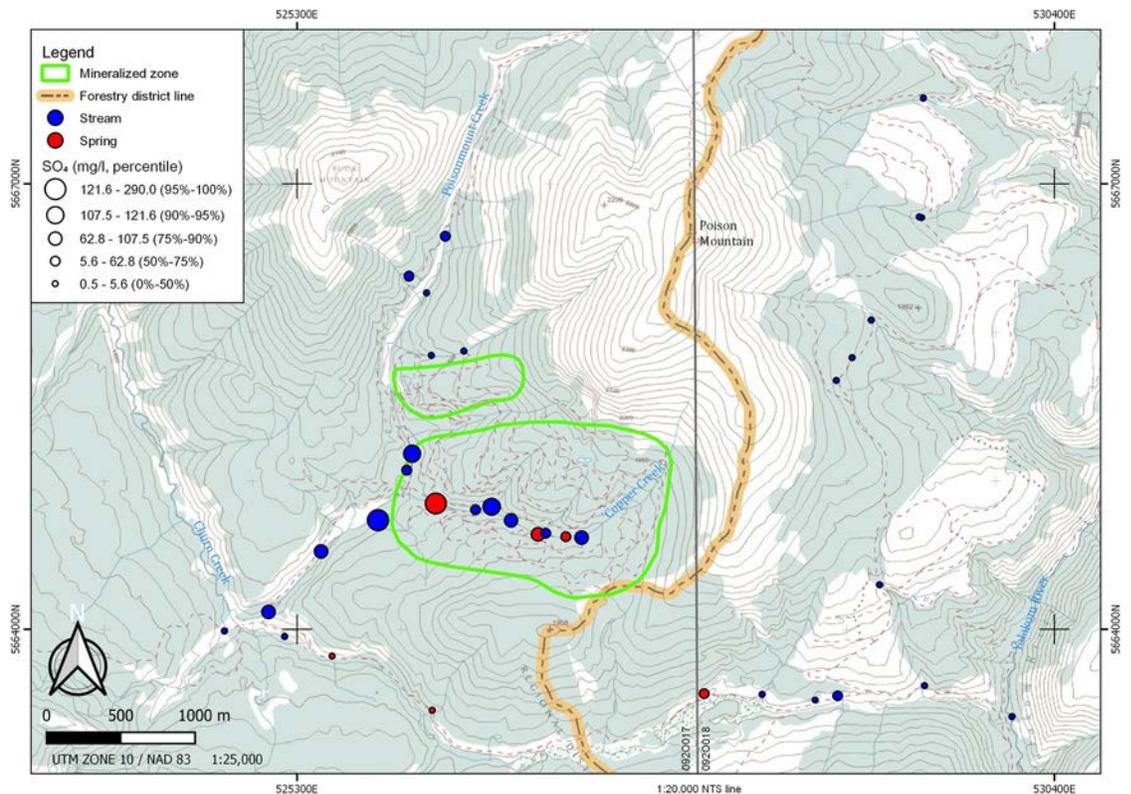


Figure 8. Report 2015-17 October photometer SO₄ results for water samples from the Poison Mountain study.

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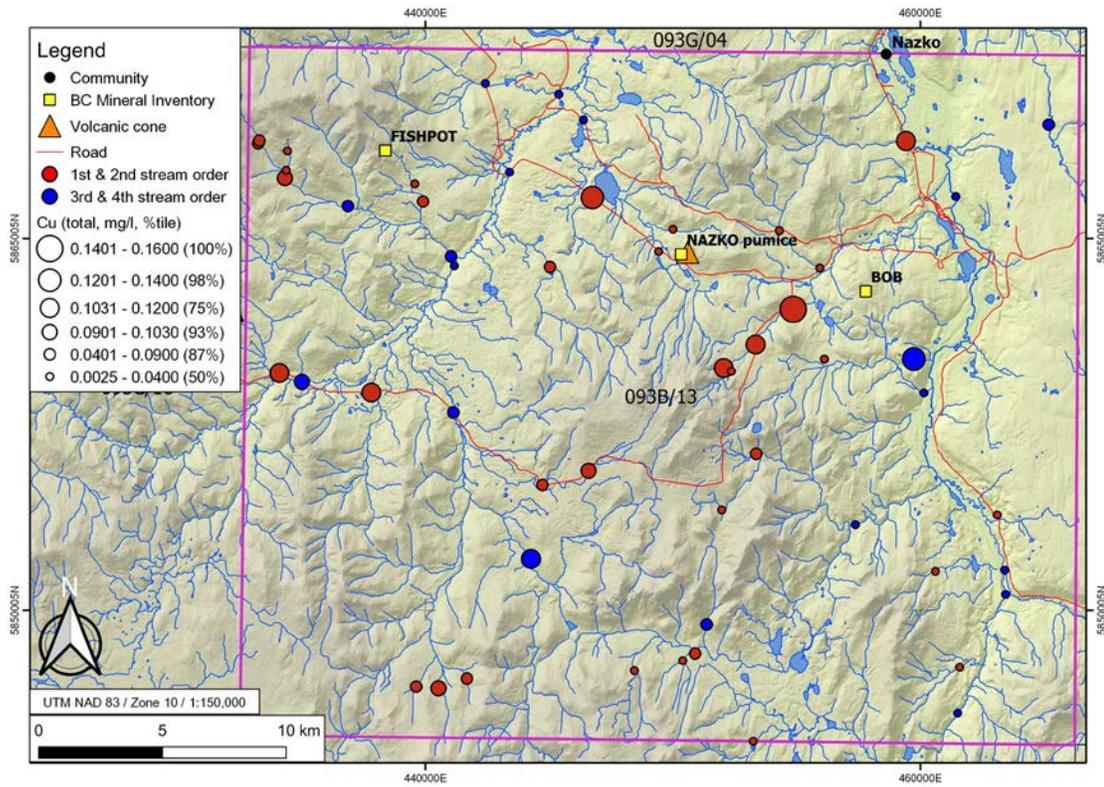


Figure 9. Report 2017-13 October photometer total Cu results for water samples from the Nazko study.

In the Nazko area, there are two drainages with elevated Cu concentrations in stream water (Figs. 9 and 10). Stream water near the Bob showing west of Fishpot lake and also in the southwest part of the survey area have elevated Cu values.

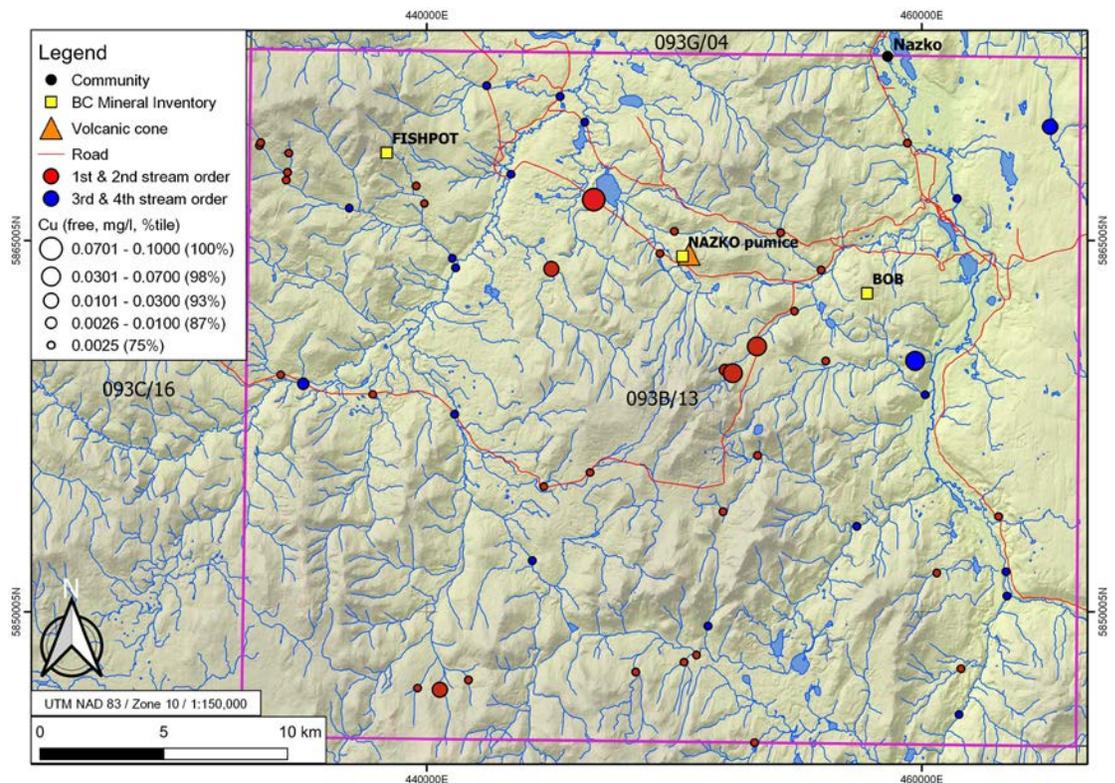


Figure 10. Report 2017-13 October photometer free (Palintest proprietary reagent terminology for dissolved Cu) Cu results for water samples from the Nazko study.

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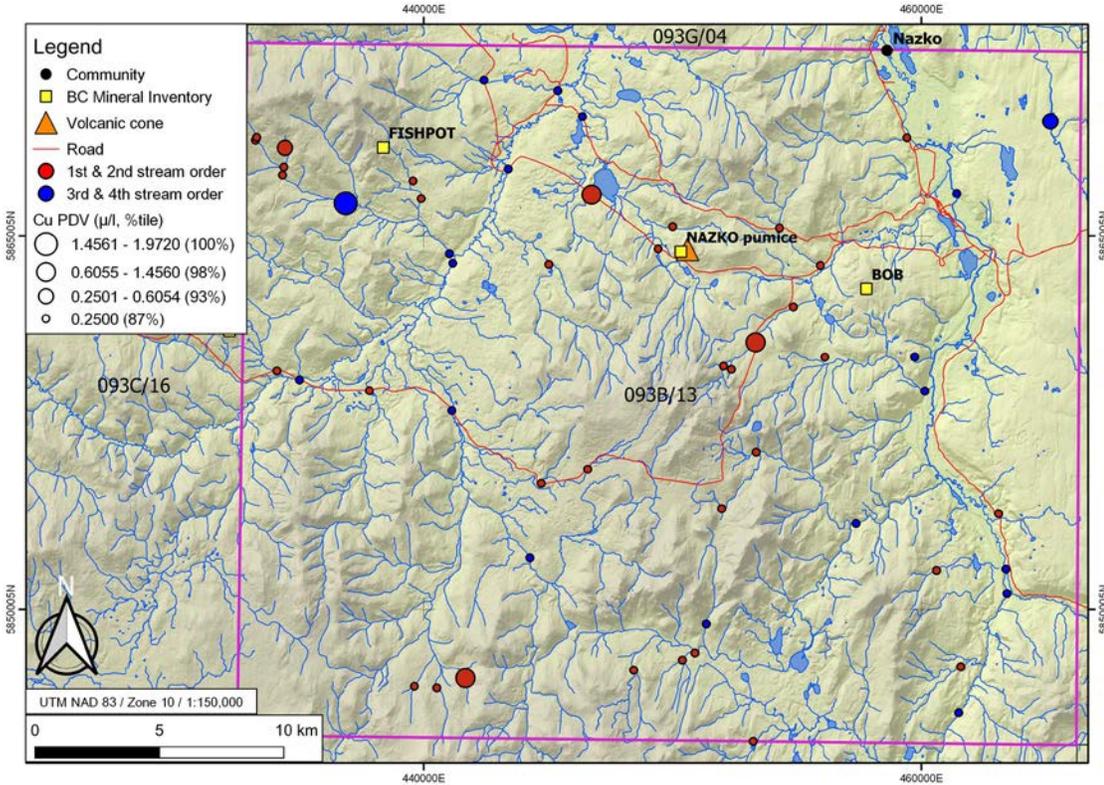


Figure 11. Report 2017-13 October voltammeter dissolved Cu results for water samples from the Nazko study. Note units are in microgram/litre.

The voltammeter (Fig. 11) was able to identify dissolved Cu in the streams due to its higher sensitivity. There is also elevated SO₄ concentrations in streams near to Bob and Fishpot and at other locations in the Nazko survey area (Fig. 12), correlating with sites of higher Cu values. Sulphate is an important indicator of sulphide weathering and the results show that, even at such low SO₄ concentrations, the photometer can possibly detect presence of sulphide mineralization.

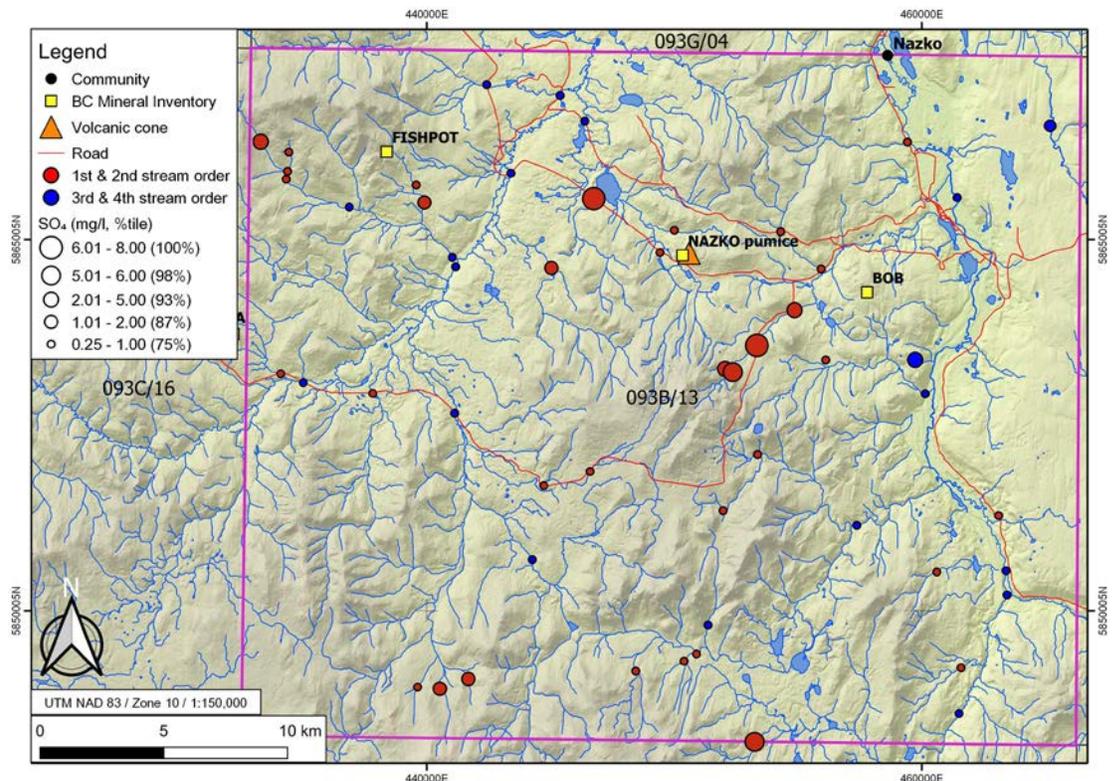


Figure 12. October photometer SO₄ results for water samples from the Nazko study.

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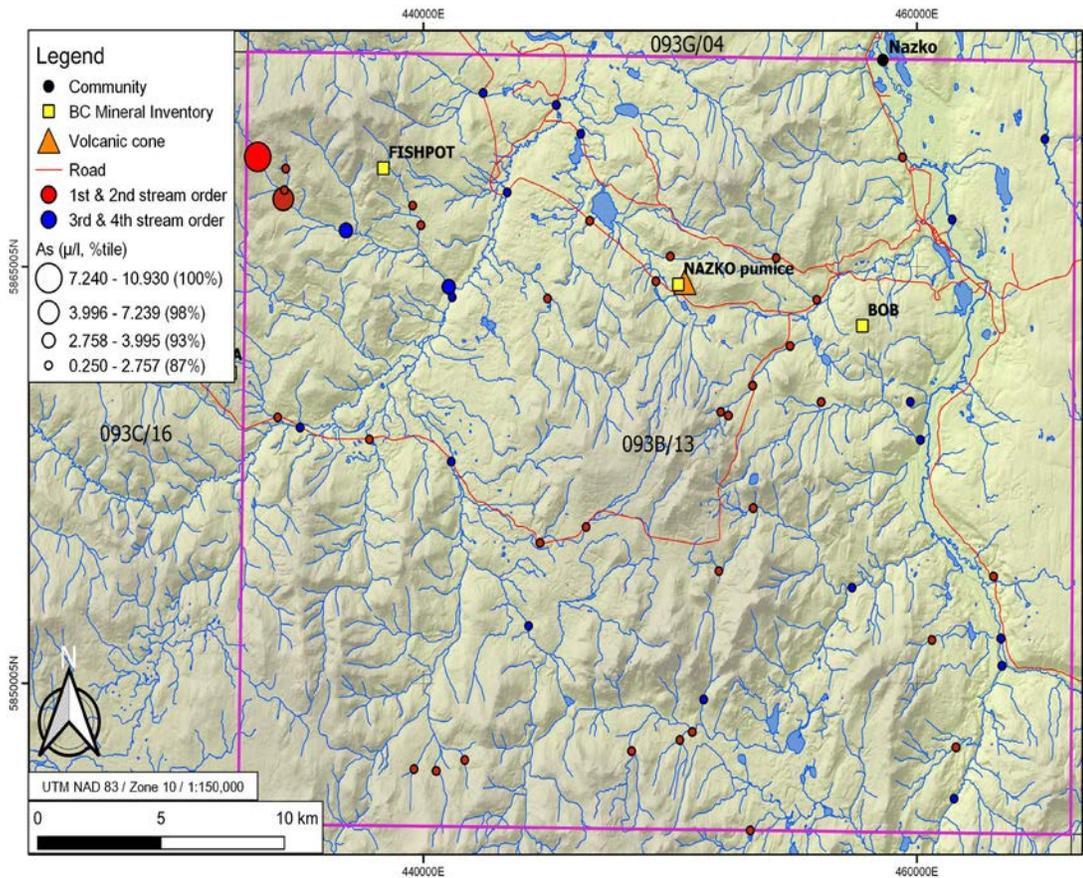


Figure 13. October voltammeter As results for water samples from the Nazko study. Note units are in microgram/litre (µg/L).

Elevated As concentrations occur in streams draining the area west of the Fishpot prospect (Fig. 13). Arsenic concentrations in water reveal a dispersion trend with decreasing values from about 10 µg/l to about 3 µg/l over a distance of about 10 km along the drainage downstream to southwest.

Discussion

The objectives of the Poison Mountain and Nazko surveys were to test the reliability of field portable devices and to provide meaningful field trace element and anion analyses of water samples. At Poison Mountain, most water samples were analysed within 24 hours of collection and at Nazko analysis was mostly completed the same day as sample collection.

The advantage of field-based analysis is its ability to determine trace element concentrations of water samples in 'near real-time'. The analyses carried out within a few hours of sample collection could allow fast identification of priority areas for immediate follow-up. The low detection limits for some analytes, e.g. photometer total (all soluble element species measured in the water) Cu (0.01 mg/l) and voltammeter dissolved (ionic species) Cu (0.0005 mg/l), provide sufficient anomaly contrast to identify sulphide mineralization at both regional and local scales. The speed of analysis using these devices provides a considerable advantage over traditional laboratory-based methods, where results may not be available for up to several weeks depending transportation and laboratory turn-around delays. The ability to make decisions while in the field can have significant time and cost benefits by eliminating the need for a second follow-up sampling campaign. The methodology applied in these studies also allows for identification and correction of errors during the survey and where necessary re-sampling problematic sample locations.

In the Nazko survey area, elevated Cu, As and SO₄ concentrations in stream water samples near to the Bob and Fishpot occurrences not only provide evidence for the presence of sulphide minerals in bedrock, but also draw attention to other areas where sulphide mineralization may be present (Fig. 14). At least two additional locations in the southern portion of NTS 093B/13 were identified during the sampling campaign that are worthy of detailed investigation.

Hydrogeochemistry is also sensitive to other factors including bedrock geology, overburden type, precipitation and weathering rates. All these processes need to be considered when interpreting the results. For example, the results of till geochemical analysis from regional surveys reported by Jackaman & Sacco (2014) and Jackaman *et al.* (2015) show spatial relationship between photometer water total Cu in stream draining the Fishpot area and elevated Cu in till assuming a regional ice flow direction from southwest to northeast. Another source of the elevated Cu concentrations

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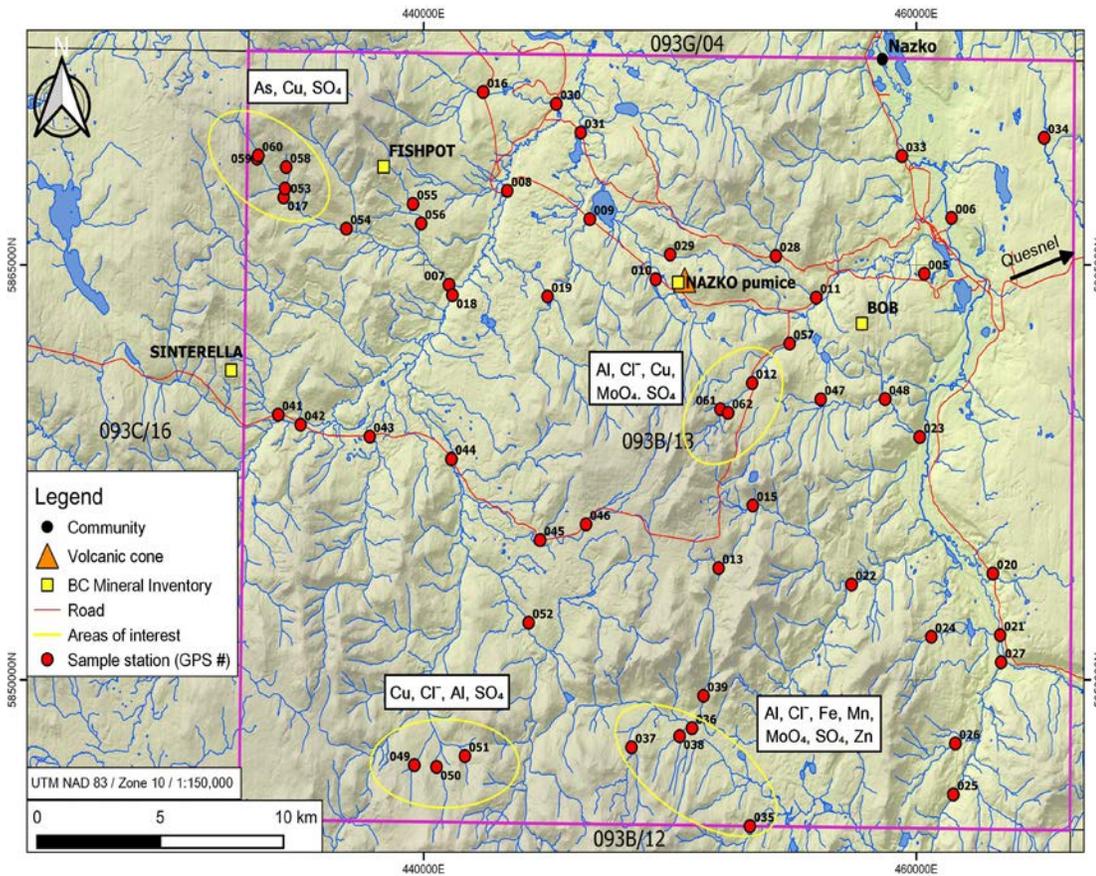


Figure 14. Identified multi-element associations in the Nazko study area.

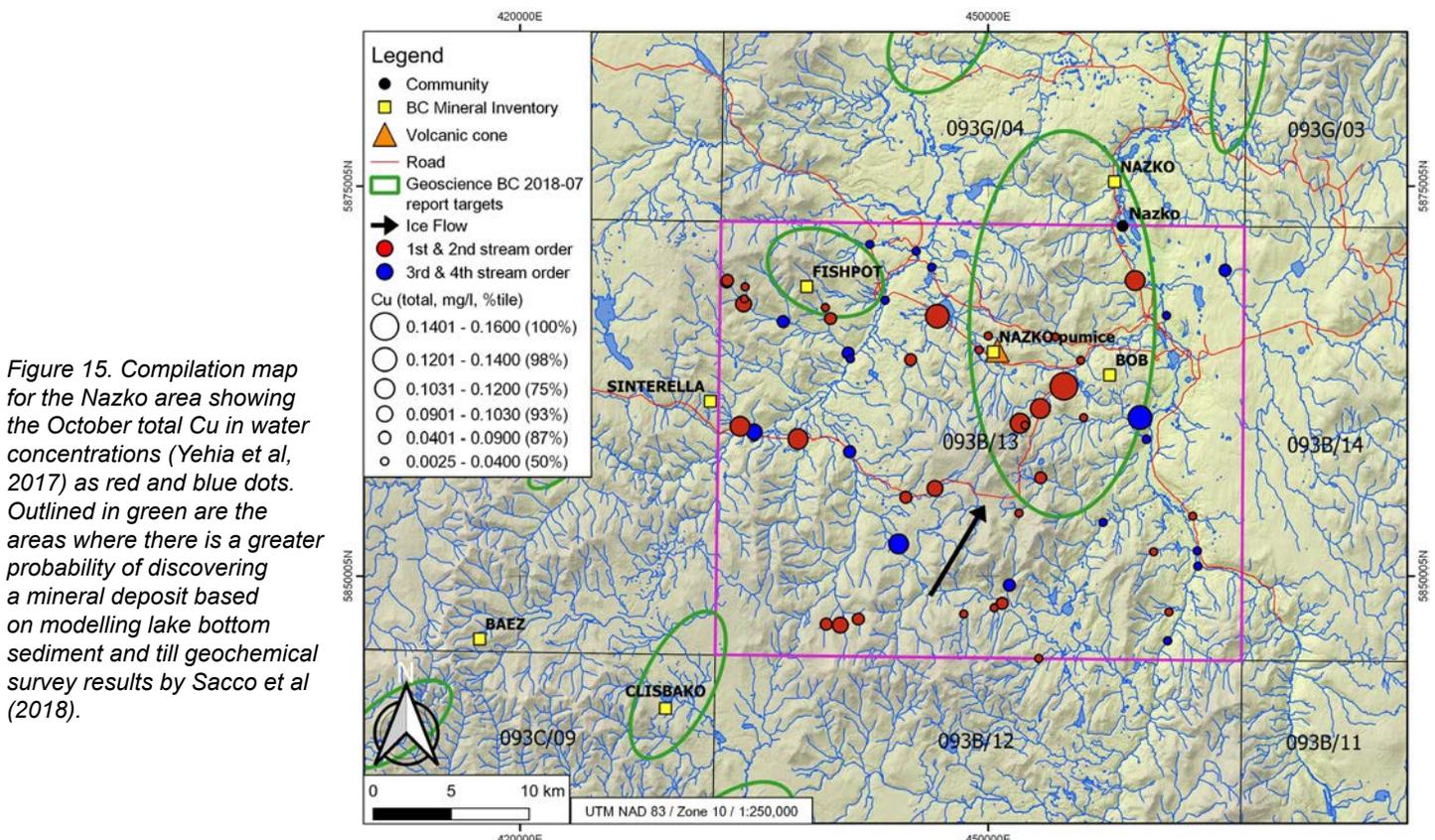


Figure 15. Compilation map for the Nazko area showing the October total Cu in water concentrations (Yehia et al, 2017) as red and blue dots. Outlined in green are the areas where there is a greater probability of discovering a mineral deposit based on modelling lake bottom sediment and till geochemical survey results by Sacco et al (2018).

in water could be Cu mineralized Eocene Ootsa Lake volcanic rocks in the survey area (Angen et al. 2015). Elevated voltammeter and photometer Cu values appear to correlate with the till Cu anomalies to the northeast of the Nazko cone, but not the Bob mineral occurrence. In fact, water samples with elevated Cu contents were collected from a stream

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about two kilometers west of the Bob occurrence. North of the occurrence, there is a spatial relationship between a till Cu anomaly and elevated Cu in the stream water. Other examples are the regions shown as green outlines in Figure 15, which are predicted to have mineral deposit types from modelling of lake and till geochemical data (Sacco *et al.* 2018). The outlines do not necessarily show the spatial relationship between water geochemical anomalies and the till geochemistry but indicate a likely common metal source. For example, the area where the till values are most elevated north of Nazko could reflect ice transport of mineralized Anahim bedrock. In the northwest part of the study area there seems to be glacial dispersal of Cu and As to the northeast (down-ice) of the Fishpot occurrence, but the principle water Cu and As elevated values appear in streams draining from the west, i.e. up-ice from Fishpot.

Cost analysis

A comparison of the relative cost per sample for both studies is presented in Table 5. The slightly higher cost for the second study was due to the addition of the voltammeter tests and need of a second assistant to operate the instrument. The results presented here show that the photometer and voltammeter can produce rapid and meaningful analyses for a suite of cations, anions and additional tests such turbidity, pH, colour, etc., at relatively low cost while in the field. The photometer and voltammeter methods are competitive with commercial laboratories that are more expensive and have much longer turnaround times. Although a rapid hydrogeochemistry suite is about 70% of a commercial laboratory suite, the field-based system does offer the ability to pick and choose the desired one; which could offer additional cost savings.

Table 5. Summary of cost per study sample for Poison Mountain (2014) and Nazko (2016) water sampling studies. Reported in Canadian dollars.

Type	Report 2015-17 cost/sample	Report 2017-13 cost/sample
Photometer reagents	\$13.14	\$10.36
voltammeter reagents	NA	\$5.32
Operational analysis	\$31.25	\$57.09
Environmental disposal	\$2.08	\$2.21
Total	\$46.47	\$75.98

Conclusions

These studies to test a field-portable photometer and voltammeter devices for the rapid analysis of water samples show that:

- The photometer and voltammeter can produce rapid and meaningful results for a suite of anions and cations at relatively low cost when compared with conventional laboratory-based methods.
- Time and cost advantages of the methodology allow increasing sample density and field follow-up during the same sampling campaign.
- There is a good comparison between various tests field analyses by the photometer and by a commercial laboratory.
- Elevated SO₄ concentrations are present in streams draining areas where there known mineralization and suggest that the method can detect the presence of sulphide minerals.

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