

# Rapid, Field-Based Hydrogeochemical-Survey Analysis and Assessment of Seasonal Variation Using a Field-Portable Photometer and Voltammeter, Marmot Lake NTS Area, South-Central British Columbia (NTS 093B/13)

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## Introduction

Water geochemistry can provide useful information in support of many resource sectors, such as mineral (Taufen 1997; Leybourne and Cameron, 2010), geothermal (Yehia et al., 2013), petroleum and environmental (Saha and Sahu, 2015). Building on the successful outcome of the 2014 project (Yehia and Heberlein, 2015) and on the wealth of data available in the TREK project area (Angen et al., 2015; Jackaman et al., 2015; Lett and Jackaman, 2015; Bordet and Hart, 2016), this project aims to extend the real-time hydrogeochemical-survey methodology to a regional setting and, at the same time, investigate the effects of seasonal variations and the potential for rapid, field-based detection of anomalous hydrogeochemistry indicative of mineral occurrences. As well, this project assesses the application of another technology for the rapid, field-based analysis of water-sample chemistry, the Modern Water PDV6000*ultra* voltammeter (PDV; Braungardt et al., 2010; Lewtas et al., 2010), an electrochemical method based on anodic stripping voltammetry (ASV).

Photometer technology and field-data-collection methodology are discussed in detail in Yehia and Heberlein (2015). This project aims to expand upon the results of that study by achieving the following objectives:

- Provide a regional-scale hydrogeochemistry dataset to supplement the QUEST and TREK SE stream-sediment, lake-sediment and till geochemical surveys in the Marmot Lake NTS area (NTS 093B/13), using field-based portable photometer and voltammeter instrumentation

- Investigate seasonal variability of water chemistry by repeating the sampling campaign in spring, summer and fall
- Investigate known mineral occurrences to determine their associated hydrogeochemical responses
- Produce accurate, precise and cost-effective analytical results for selected cations and anions that are relevant to the mineral-exploration community
- Investigate the capabilities of the PDV for rapid hydrogeochemical surveys

## Orientation Survey

One of the recommendations in Yehia and Heberlein (2015) was to carry out a small orientation survey prior to the field surveys. This orientation survey was designed to optimize sampling, sample preservation (Hall, 1998; Khanna et al., 2009) and analytical methods for the Palintest<sup>®</sup> Photometer 8000 and the PDV. It was carried out at three locations: 1) Furry Creek and Britannia Creek, which drain the Britannia mine area; 2) Lynn Creek in the Lynn Headwaters Regional Park; and 3) a creek flowing southwest of Fraser-view Golf Course in Vancouver. The sites were chosen for 1) ease of access during the spring runoff, 2) detecting potential mineralization in the water with the chosen methods, and 3) potential for mineralization comparison between laboratory and field-based water analyses. The survey included the collection of four samples at each of these localities: two filtered samples, one with acidification and a second without acidification; and two unfiltered samples, also acidified and non-acidified. Following the procedures outlined in Yehia and Heberlein (2015), duplicate unfiltered and acidified samples were sent to the ALS Environmental laboratory (Burnaby, BC) for comparative analysis.

Results from photometer tests were inconclusive in defining a single preferred sampling type for routine collection. This was due mainly to a small sample set and lower-than-expected mineral concentrations for most sites. Unfortunately, the PDV was unavailable for the orientation survey.

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**Keywords:** British Columbia, hydrogeochemistry, photometer, voltammeter, rapid, field analysis, regional geochemistry, seasonal variation

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The survey was successful, however, in identifying photometer reagents (Table 1) that seemed to have reacted adequately with the nitric-acid preservation. Further testing could be continued for Al and Fe. Previous photometer and laboratory analysis of samples by Yehia and Heberlein (2015) revealed that the photometer Al and Fe values were much lower than the laboratory analyses due to lack of water-sample preservation.

## Project Area

### Location and Access

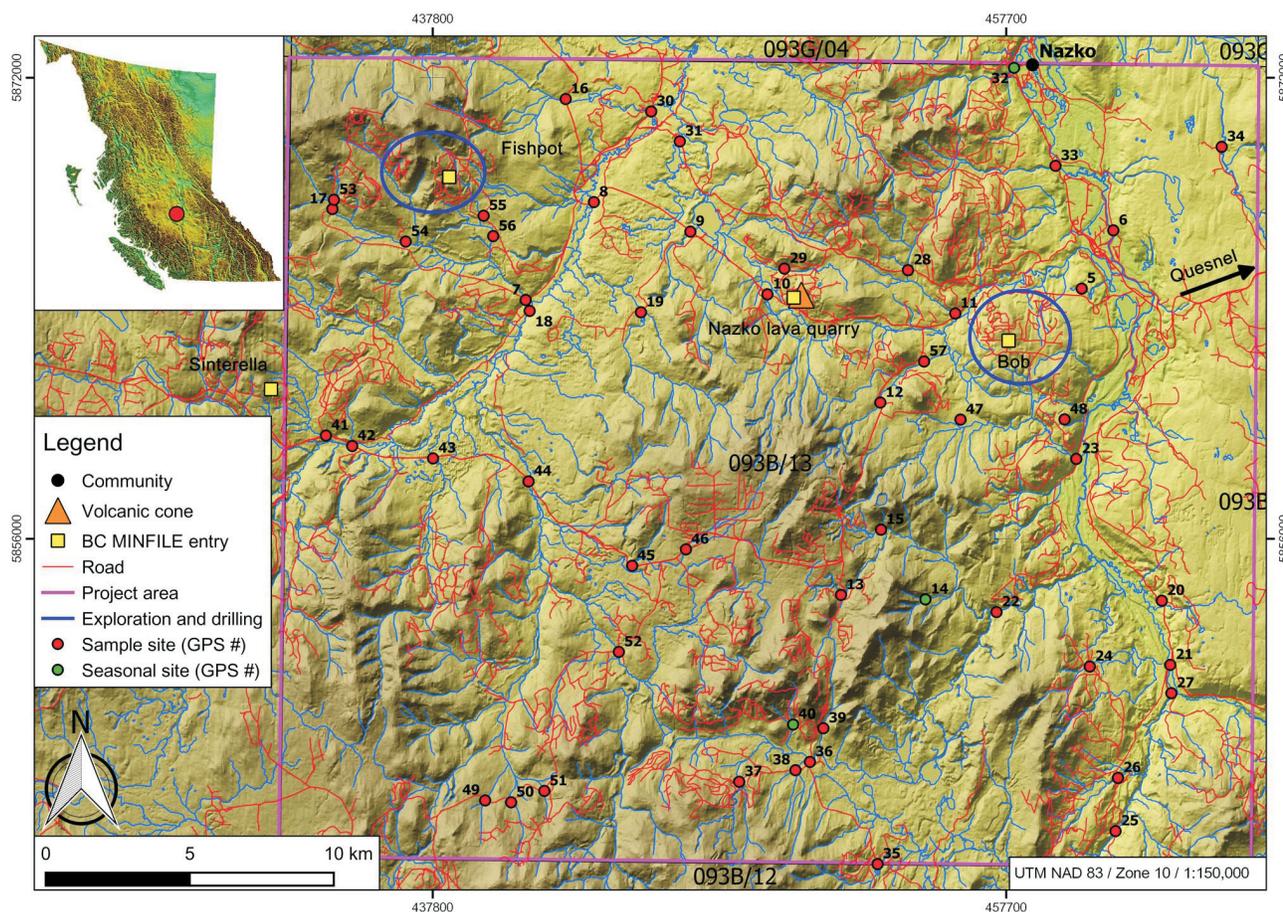
The project area is located south of Nazko (Figure 1), approximately 75 km west of Quesnel in the Marmot Lake NTS area (NTS 093B/13). As well, two mineral prospects occur in the study area, and recently collected water, soil and gas investigation data are available (Lett and Jackman, 2015) for comparison. The aim of sampling in the area was to determine if rapid hydrogeochemistry surveys will work in an environment that is hydrologically complex and challenging. In addition, the Nazko Economic Development Corporation was interested in assessing potential for resource-based economic development.

**Table 1.** Tests performed by the portable devices chosen for this project. Abbreviation: PDV, Modern Water PDV6000ultra voltammeter.

Type	Photometer detection limit (mg/l)	Typical PDV detection limit in clean water (mg/l) <sup>1</sup>
Aluminum (Al) <sup>2</sup>	0.005	
Arsenic (As)		0.0005
Cadmium (Cd)		0.0005
Calcium hardness	0.5	
Chloride (Cl)	0.05	
Copper (Cu, ionic and total)	0.005	0.0005
Fluoride (F)	0.005	
Hardness	0.5	
Iron (Fe) <sup>2</sup>	0.005	
Lead (Pb)		0.0005
Magnesium (Mg) <sup>2</sup>	0.5	
Manganese (Mn)	0.0005	
Molybdate (MoO <sub>4</sub> )	0.005	
Nickel (Ni)	0.005	
Potassium (K)	0.05	
Silica (High Range, SiO <sub>2</sub> )	0.05	
Sulphate (SO <sub>4</sub> )	0.5	
Zinc (Zn)	0.005	

<sup>1</sup>published by Modern Water Inc. ([http://www.modernwater-monitoring.com/product\\_limits-of-detection.html](http://www.modernwater-monitoring.com/product_limits-of-detection.html))

<sup>2</sup>photometer reagent capable of nitric-acid preservation



**Figure 1.** Locations of samples in the Marmot Lake NTS area (NTS 093B/13). Base map from GeoBase® (2016).

Access to the study area is via the paved Nazko Road (HW 59) and an extensive system of forestry roads throughout the project area. Elevations in the study area range from 850 to 1250 m above mean sea level. The north-flowing Nazko River traverses the eastern part of the study area. Another large river, the Baezaeko, flows from southwest to northeast in the northwestern part of the study area. The area has an abundance of water and the various types (creeks, lakes, wetlands) of water bodies, including bogs at higher elevations. Drainage patterns are predominantly dendritic. Some creeks flow in and out of wetland. A few of the wetlands are the result of beaver activity. The forest is dominated by lodgepole pine, which has been severely affected by the mountain pine beetle infestation; the resulting increase in logging activity has opened up road access to much of the area. Accommodation and logistical staging were provided partly as in-kind support from the Nazko Economic Development Corporation, and residence and laboratory space for the project crew were provided at the Blackwater logging camp.

### Geology and Surface Environment

The youngest rocks exposed in the survey area are volcanic rocks of the Miocene to Holocene Anahim volcanic belt, the easternmost limit of which is represented by the Nazko volcanic cone that erupted approximately 7200 years ago (Cassidy et al., 2011). Older volcanic and sedimentary rocks are the Miocene to Pliocene Chilcotin Group basalts along the east side of the Nazko River. Underlying the Chilcotin sedimentary rocks are volcanic rocks of the Eocene Ootsa Lake Group, which are the most extensive in the

study area, while sandstone and conglomerate of the Cretaceous Skeena Group are widespread in the northeastern part of the area, around the Bob Au-Ag prospect (MINFILE 093B 054; BC Geological Survey, 2016). Volcanic rocks of the Lower to Middle Jurassic Hazelton Group occur in the northeast corner of the study area (Massey et al., 2005). Recent mapping and an interpretation of airborne geophysical-survey data by Angen et al. (2015) revised the geology of the project area and identified several new faults, including an inferred dextral fault along the Nazko River valley.

The area has an abundance of glacial deposits of various thicknesses, till being the dominant surficial material that overlies much of the bedrock. The most recent ice-flow direction in the area is generally from south-southwest to north-northeast (Jackaman et al., 2015).

In the northwestern part of the study area, Cu-As-Au mineralization at the Fishpot showing (MINFILE 093B 066) is hosted in an Eocene pyritic quartz rhyolite porphyry plug that intrudes Late Jurassic Hazelton Group pebble conglomerate, shale and tuffaceous sandstone. The Hazelton volcanic sequence consists mainly of andesitic and basaltic flows, and lesser amounts of pyroclastic rocks. Two major alteration zones identified on the prospect consist of carbonate-limonite staining and local quartz veining (Kennedy, 2012).

The Bob prospect, which has been more thoroughly explored, lies just south of Nazko and east of the Nazko volcanic cone. It is underlain by Lower Cretaceous to Lower

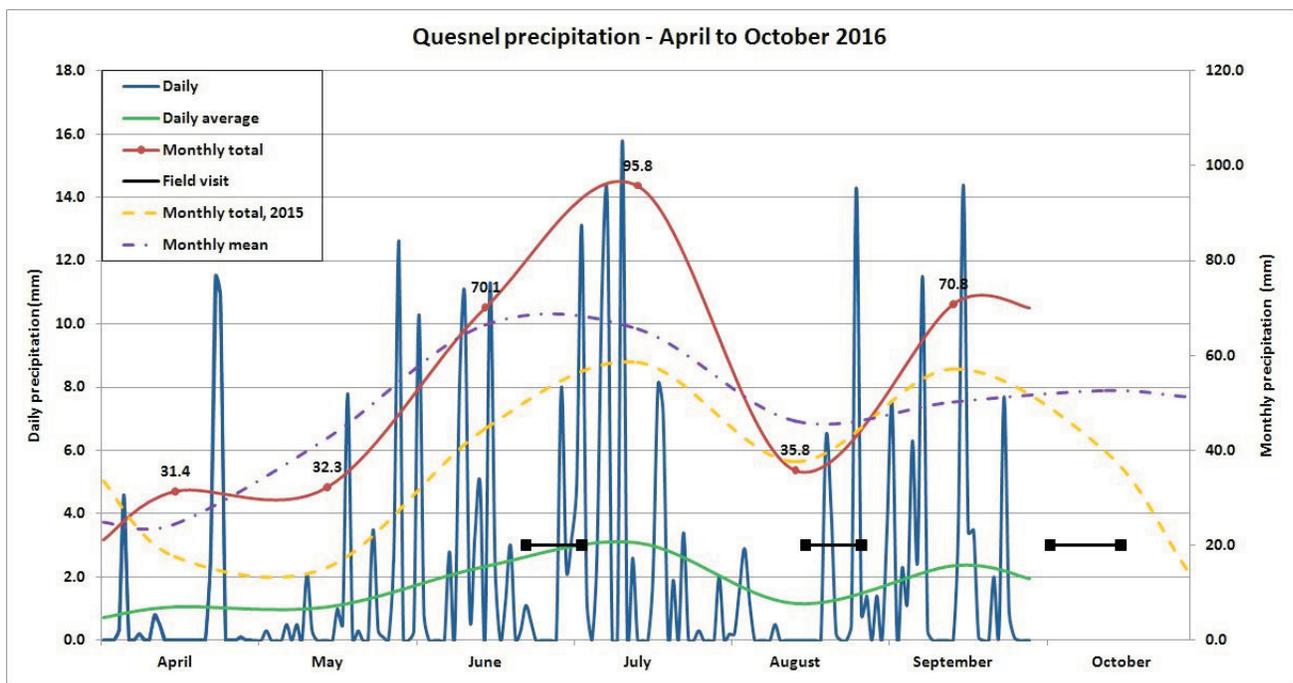


Figure 2. Precipitation for Quesnel at the time of the sampling campaign (Environment Canada, 2016).

Paleogene Skeena Group conglomerate, sandstone and argillite that are unconformably overlain by Paleocene to Eocene andesite, basalt, basalt breccia and rhyolite breccia. Tertiary quartz-feldspar porphyry dikes intrude the Skeena Group sedimentary rocks. Anomalous Au, As, Ag, Sb and Hg levels have been reported from Skeena Group sedimentary rocks that have undergone silicification and argillic alteration, and contain carbonate minerals and pyrite (MIN-FILE 093B 054).

### Field Conditions

Although precipitation in the month of June for the last couple of years had been below the mean of 66 mm, the June sampling campaign was carried out under wet conditions. Precipitation recorded for Quesnel in April and May had been 25 mm, but totals for June and July were 56 and 82 mm, respectively (Figure 2), with potentially more precipitation noted in the Nazko area (Nazko is 600 m higher than Quesnel). June's precipitation turned creek water turbid with high or overflowing banks, a noticeable change from the previous two months.

Vehicle access to some parts of the area was complicated by widespread mud on the secondary logging roads, and foot access was complicated by high water levels in creeks and wetlands. This made sampling at some sites and subsequent follow-up challenging. Conditions were drier in August compared to July, but water levels were still above average because of July precipitation. Regardless, road and foot access was markedly improved from the June campaign.

### Sample Collection and Analysis

Water samples were collected directly from mid-stream sites; where streams were too wide or the banks unsafe, samples were collected using a water-sampling pole. Samples were stored in two sizes of #2 high-density polyethylene (HDPE) bottles: non-acidified samples in 1 L bottles and acidified samples (with 3 mL ultrapure nitric acid) in 250 mL bottles. Both samples were unfiltered. Sample bottles were reused and rinsed thoroughly three times with the water to be sampled, with the cap on before sample collection. Collected water was transported in a cooler after collection and stored in a refrigerator at the camp until analysis (except for some samples that were analyzed the same afternoon). Analysis was carried out within 24 hours of collection for both photometer and PDV (within 48 hours in the orientation survey). Sample locations were tested for temperature, pH, conductivity, total dissolved solids (TDS) and salinity using an Oakton PCStestr 35 meter. The samples were retested as a quality-control procedure with a second PCStestr for the same parameters prior to analysis to prevent sample mix-up and record any changes after collection. Both meters were calibrated weekly. No unusual differences were observed between the two sets of results, except for the expected slight pH variations and normal

analytical variations caused by using a different instrument.

Identical procedures were used for samples sent to the ALS Environmental laboratory, except for filtering on site for dissolved-metals analysis. Dissolved tests involved filtering the sample through a 0.45 µm filter and preserving the metals in the solution with 3 mL nitric acid. Water in the 250 mL bottles was used for cation analysis, whereas the 1 L sample was required by the laboratory for TDS determination, conductivity, turbidity, anion analysis, quality-control monitoring and reanalysis (if required). Water samples for laboratory analysis were transported in coolers to the ALS Environmental laboratory in Burnaby by the lead author the day after returning from the field trips. Laboratory determinations were for dissolved constituents, since both photometer and PDV measure the dissolved component of the sample (except for the photometer Cu test, which analyzes for ionic Cu as well as total dissolved Cu—after reaction with a decomplexing agent).

The number of sites sampled around mineral occurrences turned out to be lower than initially estimated. This was due to the lack of suitable sample sites draining directly from the Bob prospect and inactive (dry glacial outwash) channels around the Fishpot showing. A second stage of sampling involved follow-up around both mineral occurrences, as well as more regional sampling over the broader NTS area. Sample sites for the latter were chosen for their safe access from the primary logging roads in spring, due to the high water levels.

### Quality Control

Quality-control measures used for the project included

- use of the manufacturer's standard solutions and government-certified reference solutions for calibration and drift monitoring;
- triplicate readings for each photometer test, which helps to monitor analytical precision as well as identify any reagent problem; and
- for every batch of 20 samples, the following:
  - 15 field samples
  - 1 field duplicate
  - 1 analytical duplicate (second test from same sample bottle)
  - 1 government-certified standard
  - 1 blank using ultrapure deionized water (18 MΩ)
  - 1 laboratory duplicate for every tenth sample.

### Analysis

Table 2 shows the samples that had been collected and analyzed by the time this paper was written. In the June survey, the photometer analyzed many samples with high turbidity (tested by the photometer), whereas previous surveys

**Table 2.** Sampling completed to August 31, 2016.

Type	Sampled and tested	Laboratory samples
Orientation survey	4 sample sites (16 tests) 1 deionized 1 SLRS-6 Standard	4
June field survey	49 sample sites 3 deionized 3 SLRS-6 Standard 3 analytical duplicates 3 field duplicates	8
August field survey	50 sample sites 3 deionized 3 SLRS-6 Standard 3 analytical duplicates 3 field duplicates	5
<b>Total</b>	<b>141</b>	<b>17</b>

(Yehia et al., 2013; Yehia and Heberlein, 2015) included only a very few turbid samples. Reagents that did not involve a high-wavelength colour test (Figure 3), such as Cu and MoO<sub>4</sub>, appeared to be affected by the higher turbidity levels. As the photometer uses light to analyze the samples, higher turbidity levels appear to produce a high bias in the measured concentrations.

Figure 4 shows examples of the influence of turbidity on the June Cu and MoO<sub>4</sub> results. Both analytes display strong positive correlations with turbidity in the photometer results (left), but this effect is not reproduced in the corresponding laboratory turbidity analyses (right). Variations in turbidity are likely to cause a similar trend in the laboratory results.

The photometer uses a separate tube as a ‘blank’, against which all reagent tests are compared. In the past, the pho-



**Figure 3.** Collection of reagents ready for photometer testing. Note the clear Cu test (third from the left) that could be susceptible to turbidity interference, which occurs when the photometer records a false concentration because the solution is darker due to turbidity.

tometer tests used deionized water for the blank, as it was a method of measuring maximum turbidity differences between the clear water and the sample. Palintest states that, when turbidity is below 10 Formazin Turbidity Units (FTU), the turbidity test is not as precise as can be achieved with a dedicated turbidity meter (Palintest, pers. comm., 2016). At these low turbidity levels, reagent tests, including the clear-water ones, should not be affected by the turbidity. Palintest further states that, when turbidity is between 10 and 80 FTU, test accuracy is adequate and should not affect the results. Following consultation with Palintest and further field tests in August, it was decided to follow Palintest’s recommendations for using filtered sample water for each suite and continuing with the deionized water blank for turbidity monitoring. Using filtered sample water as a blank counteracts the turbidity effect to try and keep FTU below 10 for accurate reagent results. Initial testing and photometer analysis for elements in August is promising, and more comprehensive analysis of water samples is ongoing.

The PDV was included in the June and August surveys. The team had to overcome some initial challenges with the instrument in June. Some of the issues were related to outdated Modern Water documentation (initially supplied with the device) and a high learning curve for the device operators during the actual survey, since the PDV was not available before the survey to allow adequate training time. Consequently, testing was limited to just As, Cd, Cu and Pb. Lengthy preparation time required for analysis of each element suite also prevented the team from performing additional tests, such as Zn or Mn.

## Conclusions and Recommendations

Preliminary observations from the program so far are as follows:

- The rapid nature and low cost of this field methodology can allow for higher density surveys, thus
  - enabling increased sampling of first- and second-order streams, closer to the stream source or groundwater influx; and
  - offsetting lower concentrations in samples during times of higher precipitation (e.g., some follow-up was already possible during the short field-survey time for this project due to the rapid nature of the methodology).
- Differences were recorded between June and August in field observations with higher TDS, conductivity, etc., and higher concentrations in analytical results in August. These observations will be incorporated into the seasonal variation analysis.
- For a large survey, the PDV requires a controlled, logistically convenient operating environment because

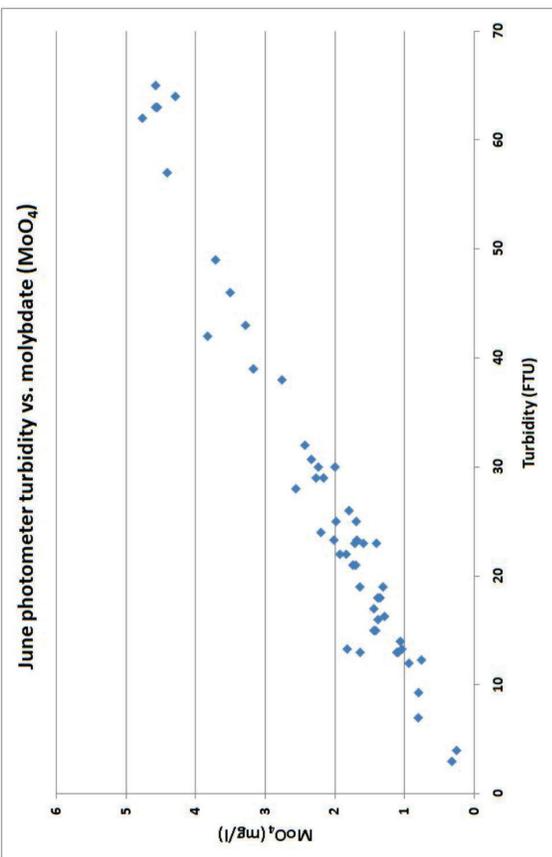
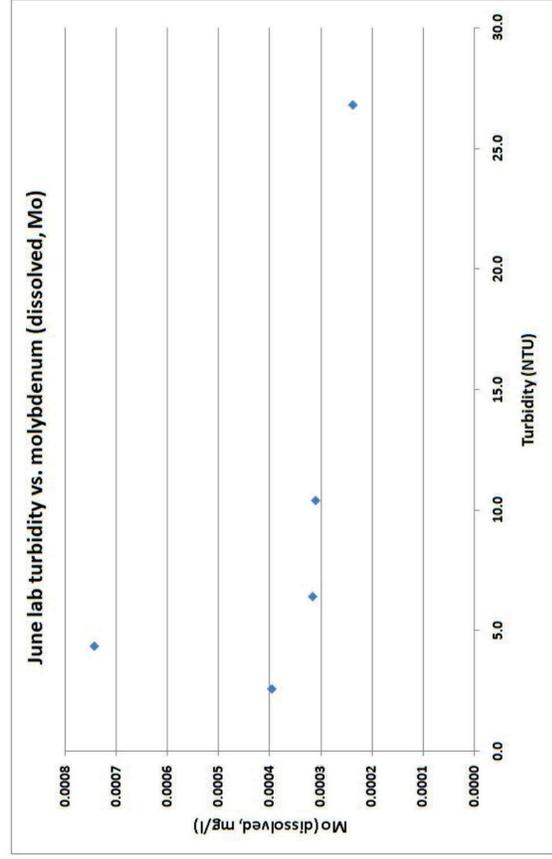
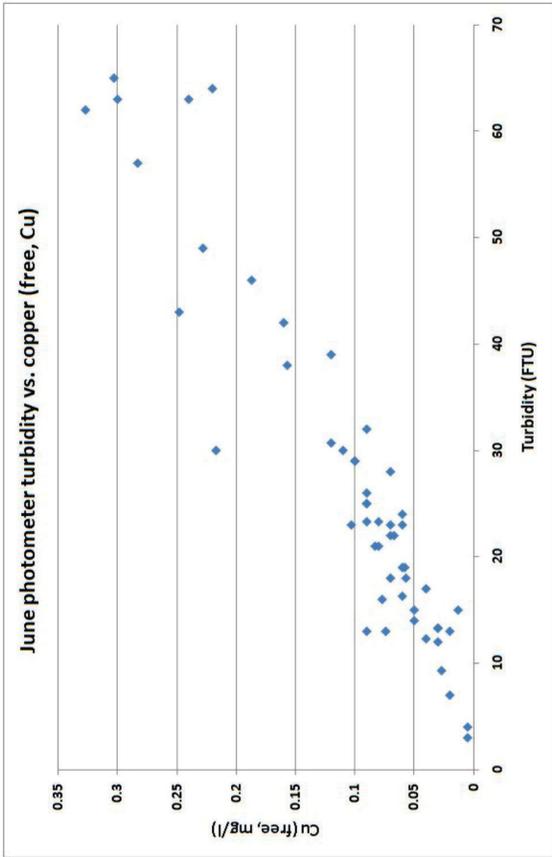
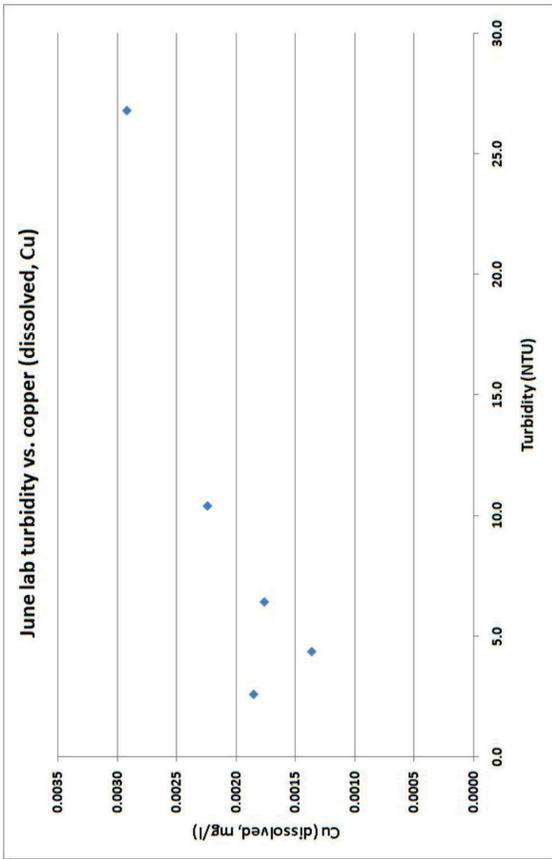


Figure 4. Scatterplots showing the potential for turbidity effect on element concentrations determined by photometer analysis (left) and laboratory analysis (right). Note the negative turbidity versus concentration correlation in the plot of Mo laboratory concentrations (bottom right).

- each analyte suite requires a certain amount of preparation time. For large sample sets, any technical difficulties encountered during that time cause significant delays and analytical backlog.
- lack of a Canadian distributor and technical support caused delays and supply difficulties, and is an issue to consider for surveys under a strict timetable.
- unlike the photometer, a higher technical skill level and additional training time are required.
- The PDV has the ability to detect concentrations at much lower levels than the photometer, and offers additional cation tests that the Palintest photometer does not include (Table 1).

### Continuing Fieldwork

The lead author returned to the project site in October for repeat sampling at the time this paper was written. Once all of the data has been analyzed, the following reporting is planned:

- final report documenting methodologies used
- discussion of data quality and description of results
- set of digital maps showing concentrations of the measured analytes
- digital database of the analytical and quality-control results

The project is expected to be complete in early 2017, at which time a final report will be submitted to Geoscience BC.

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