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Use of a Portable Photometer for Accelerated Exploration: Testing for Geothermal Indicators in Surface Waters

Ron Yehia[1], Nathalie Vigouroux[2], and Catherine Hickson[2]

[1]Exploration & Data Consultant, Vancouver, B.C., Canada
[2]Alterra Power Corp, Vancouver, B.C., Canada

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ABSTRACT

When exploration budgets are limited, cost-effective surveying techniques can add considerable value to an exploration program by increasing the return on investment. In western (British Columbia and the Alberta cordillera) and northwestern (Yukon and Northwest Territories) Canada, where water is abundant, sampling creeks, streams and springs and testing the waters for geothermal indicators can facilitate identification of thermal zones both regionally and locally around known hot springs. Such a sampling program can be rapidly and easily accomplished using a photometer, which provides chemical analysis of waters in real-time, enabling the survey team to evaluate and optimize a survey during the course of the field work. With this technique, suspected thermal springs and seeps can be verified and new ones discovered, allowing for the rapid identification and characterization of thermal anomalies. The cost and time associated with this technique is a fraction of what is required when employing traditional laboratory analysis. A pilot test, performed in the area surrounding Mt. Cayley in southwestern British Columbia (BC), concludes that despite some issues with instrument sensitivity at low concentrations the device provides feasible data for a surface water survey and promises to be an effective tool for the rapid identification of thermal anomalies.

Introduction

Exploration in western Canada poses unique challenges; remote areas with limited access, thick foliage, steep topography, high levels of precipitation and short exploration seasons are some of the challenges. These factors contribute to increased operational costs and time required to conduct field investigations. While most major hot springs in BC have been identified, finding any new thermal springs or seeps can present an arduous task.

Currently available techniques for regional identification of areas of interest can be time and cost intensive. Remote sensing techniques such as surface radiance mapping using ASTER satellite data, mineralization mapping using hyperspectral imaging and thermal anomaly mapping using FLIR do not effectively "see through" thick canopy. Furthermore, publicly available regional datasets from soil and surface water chemistry surveys, fail to report data on the geochemical indicators or have detection limits that are too high.

British Columbia has an abundance of surface water that can be used advantageously for geothermal exploration. Sampling of streams and creeks and testing for geothermal chemical indicators can pinpoint places for further investigation (e.g., Ryder, 1983). Ryder (1983) performed an initial survey of this type around Mount Cayley with promising results. Mount Cayley is a Holocene volcano in southwestern BC with known hot springs. Executing this type of survey in the traditional manner and sending all water samples to a laboratory for analysis is expensive and time consuming.

Figure 1. Set-up and equipment needed for photometer analysis in the field. The Palintest Photometer 8000 is the blue and white device at the bottom right of the picture.

A portable photometer can be used for preliminary analysis of waters in the field, allowing for more cost-effective targeting of areas of interest. The initial investment cost for a photometer device, including reagents and accessories, is \$4,000 - \$5,000 USD. Photometer analysis costs are based on the cost of reagents, which translates to a cost per sample equal to one tenth the cost of a laboratory analysis. During the 2012 summer field season, Alterra Power's exploration team tested this new methodology successfully despite some initial challenges discussed below.

Methodology

Instrumentation

The device chosen for the pilot survey was the Photometer 8000 by Palintest (examples of other manufacturers are YSR and HACH). This photometer was chosen for its large selection of reagents and chemical analyses, its low detection limits, and its light-weight portability (1.65 kg), having both an AC and DC power supply. This portability enables ground teams to transport the device easily and perform tests on site (Figure 1). Three common geothermal chemical indicators were tested for: chloride (Cl^-), sulphate (SO_4^{2-}) and total dissolved silica (Si, expressed as SiO_2). At the low concentrations of Si found in these surface waters (maximum 16 ppm SiO_2), precipitation of silica was not a concern, however we did test for the effects of precipitation by collecting a duplicate sample that we treated with acid to preserve the dissolved silica concentration. Additionally, magnesium (Mg) was included in the suite of tests as a control, as Mg is not commonly associated with geothermal fluids. The combination of these four tests allows us to distinguish geothermal waters from other mineralized waters. Finally, despite filtering the waters prior to analysis, we measured their turbidity in order to identify any influence on the photometer test results.

Prior to field deployment, initial tests were conducted with Palintest calibration fluids as well as local tap and stream water for which public data was available for comparison. After assuring good comparison with the public water quality records and acceptable reproducibility of the results, the device was deemed suitable for field testing.

Field Site and Sampling Protocol

The Mount Cayley area was chosen for this pilot project because it was a target site for geothermal exploration back in the early 1980s. In 1982, a hydrogeochemistry survey was conducted along the SW flank of the volcanic complex in order to identify anomalously mineralized surface waters associated with geothermal fluids upstream (Ryder, 1983; Figure 2). Results from this survey provided historical data for comparison with our survey. For each sample site, one sample was tested using the photometer and an additional sample was sent to the ALS Environmental lab in Vancouver for analysis. Comparison between the photometer and laboratory results provides a measure of the photometer's accuracy. Precision of the various photometer tests was evaluated using a minimum of three repeat measurements. Photometer analysis was carried out within 24-48 hours of sample collection. Repeat analyses were carried out one month after sampling in order to investigate factors such as instrument drift and sample preservation.

To test for seasonal variations in the water chemistry, a second round of sampling was done in late fall when water levels were supposed to be at their lowest and the concentration of geothermal indicators at their highest. The concern was that high water levels during the summer of 2012 (due to the melting of a record snow pack) might have diluted the samples to concentrations below the detection limit of the photometer. Additionally, these repeat samples allowed us to evaluate any change in the ratio of the species (e.g., Cl^-/SO_4^{2-}) over time. Water flow rate estimates were made during both the summer and fall surveys.

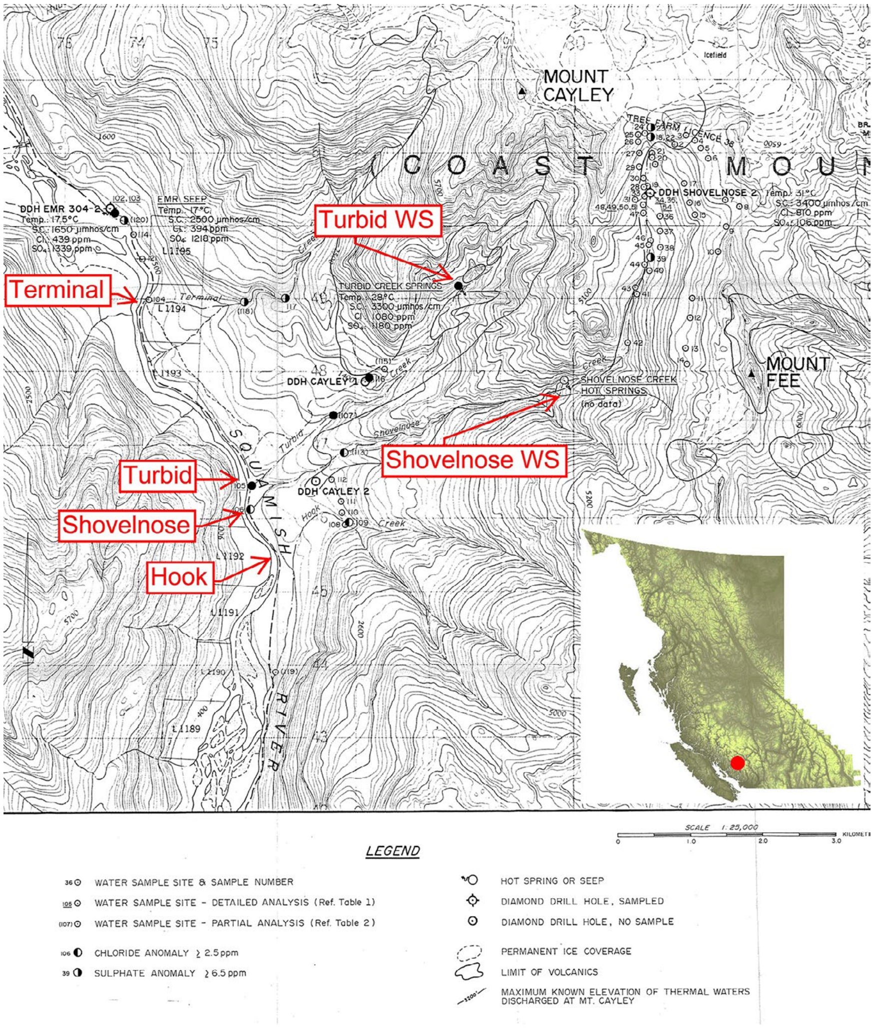

Figure 2. Map showing the location of Ryder's sample points around the SW flank of Mount Cayley (map modified from Ryder, 1983). The 2012 samples were collected from the four creeks on the SW flank of Mount Cayley (labelled Terminal, Turbid, Shovelnose and Hook), just upstream from where they cross the Squamish Valley road before draining into the Squamish River. The location of the Turbid and Shovelnose warm springs (WS), higher up on the flank of Mount Cayley, is also indicated. High Falls creek, also sampled in 2012, is located approximately 12 km south of Hook creek (not shown on map).

Table 1. Photometer and laboratory results for both the summer and fall 2012 sampling campaigns, along with estimated creek flow rates. Each photometer data point is an average of at least 3 repeat measurements. All results are in ppm unless noted otherwise. August chloride results are missing. August sulphate data for Terminal Creek is omitted. See text for details.

Lab SO4	Photometer SO4		Lab Mg	Photometer Mg		Lab SiO2	Photometer SiO2		Lab F-	Lab B	
	Aug analysis	Sept analysis		Aug analysis	Sept analysis		Aug analysis	Sept analysis			Est. Discharge Rate (L/s)
2.65	-	18.00	0.58	0.33	0.33	5.07	4.93	4.40	<0.020	<0.010	3,650
72.50	85.67	83.00	18.90	23.00	26.00	14.8	15.00	7.80	0.159	0.260	285
1.26	11.67	16.00	0.60	5.00	0.67	4.96	5.60	2.20	<0.020	<0.010	9,900
2.56	17.00	14.67	0.44	1.50	1.00	7.55	8.53	3.33	<0.020	<0.010	3,200
0.94	22.33	11.33	0.12	2.33	1.00	3.17	2.95	3.00	<0.020	<0.010	4,000

Lab SO4	Photometer SO4		Lab Mg	Photometer Mg		Lab SiO2	Photometer SiO2		Lab F-	Lab B	
	Oct analysis	Nov analysis		Oct analysis	Nov analysis		Oct analysis	Nov analysis			Est. Discharge Rate (L/s)
5.38	24.67	9.33	1.01	1.33	0.33	7.20	7.20	6.23	0.026	<0.010	660
95.10	91.67	118.00	20.30	25.00	28.67	14.47	13.83	15.03	0.167	0.260	815
2.47	24.00	8.67	1.06	3.67	0.00	8.70	6.60	9.37	<0.020	<0.010	7,050
2.44	25.67	6.00	0.40	1.67	0.00	6.27	5.47	6.67	<0.020	<0.010	3,700
1.20	24.67	7.67	0.17	0.67	0.33	3.68	3.60	3.62	<0.020	<0.010	2,650

Water temperatures were measured on site using pocket thermometers and an Oakton Testr 35 digital multi-parameter reader. The Oakton was also used to measure pH, conductivity, TDS and salinity. Additional pH and Cl$^-$ concentration measurements were made using Quantab Cl$^-$ strips and Aquacheck pH strips, both from HACH. For the calculation of the volumetric flow of water, average creek width, depth and surface flow rate were measured (Table 1).

Samples for both photometer and ALS laboratory analysis were collected in 1 L plastic bottles provided by ALS. Each bottle was first rinsed at least twice with the sample water. All samples were filtered using a 45 micron filter. For inorganic water chemistry analysis by ALS, 1 L of filtered water and 250 mL of filtered and acid-treated water (using HNO_3 for SiO_2 preservation) was collected. During the fall sampling campaign, an additional 250 ml water sample treated with HNO_3 was collected for photometer analysis a month later and comparison with the non-treated sample. During photometer analysis, water temperature, pH, conductivity and TDS were measured using an Oakton 300 Series digital multi-parameter meter.

Each photometer test was conducted following the specific instructions provided by Palintest. Initially, we assumed that SiO_2 concentrations in the creeks would be low, but in about 75% of the samples SiO_2 concentrations were higher than 4 ppm (maximum for low range silica reagents) and a dilution factor had to be applied. Results were recorded both manually and saved in digital format by the photometer software. The two records were compared for quality assurance.

During the fall sampling campaign, rainfall of at least 40 mm fell the week prior and continued intermittently during the campaign. Even though water levels were not at their lowest, we proceeded with the campaign in order to test the effect of dilution by rainfall. In order to limit the dilution effect, sampling was performed at least 12 hours after each rainfall (when creek water levels had receded to some extent).

Results

Representative results of the photometer analyses in the Mount Cayley area are presented in Table 1. During the first round of photometer analysis in August we did not have access to the correct reagent for chloride determination, therefore chloride results are only reported from September onwards. Additionally, August sulphate results for Terminal Creek are omitted because the proper preparation procedure for the test (vial shaking) was not performed.

Table 2. Chemical composition of the downstream waters and the warm springs at Mount Cayley. Data from Ryder (1983) and Dellechaie (1984).

Creek	Cl$^-$	SO4	Mg	SiO2	F$^-$
Terminal	0.50	5.56	0.95	11.60	<0.030
Turbid	71.30	69.50	17.80	22.60	0.080
Shovelnose	22.10	3.43	1.41	15.80	<0.030
Hook	1.82	3.55	0.69	-	-
Turbid WS	**1080**	**1180**	**168**	**91**	-
Shovelnose WS	**787**	**60**	**13**	**45**	-

Table 3. Total number of photometer analyses recorded in 2012, after QA-QC, and incorporated into the data analysis of this report. On average, three individual analyses were recorded per test. The complete data set was used for the statistical analysis, but this paper discusses the results from Cayley only.

	Sample Locations	Samples Collected	Individual Data Points	Test
Overall	**24**	**39**	**183**	**Turbidity**
			258	**Chloride**
			336	**Sulphate**
			334	**Magnesium**
			326	**Silica**
Total			1437	
Cayley	5	10	60	**Turbidity**
			76	**Chloride**
			97	**Sulphate**
			96	**Magnesium**
			96	**Silica**
Total			425	

Sources of Error, Precision and Accuracy

In order to perform a comprehensive analysis of the precision and accuracy of the photometer data, all of the survey data collected during the 2012 field campaign (not just Mount Cayley) was used (Table 3).

Sources of Error

A source of random error was discovered when analyzing the SO_4 photometer results and comparing them to the lab results. Instructions for the SO_4 test included the guideline to 'shake before reading'. However, test results showed that individual readings varied depending on how vigorously the vial was shaken and this was particularly apparent at low SO_4 concentrations. Aquatic Life Ltd., the Canadian distributer of the Photometer 8000, clarified that a specific stirring tool should be used and that the vial should not be shaken but stirred. This issue was not resolved until the last round of testing in November, the results of which are considered to be the most reliable. Some unresolved accuracy issues with respect to SO_4 are discussed further below.

Table 4. Photometer precision and accuracy reported as average relative standard deviation (%) and relative error (%) (lower values are better). Data is post QA/QC. The removal of outliers is described in text.

Test	Relative St. Dev. (Av.)	Relative St. Dev. (BD and outliers omitted)	Relative St. Dev. (Turbid only)	Relative error (Av.)	Relative error (BD omitted)	Relative error (no precipitation)	Relative error (Turbid only)
Turbidity	**26.58%**						
Cl^-	**24.04%**				**23.13%**		
SO_4	**6.28%**			**623.75%**			
SiO_2	**2.41%**			**30.24%**		**26.35%**	
Mg		**37.97%**	**1.20%**	**237.11%**			**23.57%**

Another source of error, which may be systematic, involved the Cl^- test. The Cl^- test available with the Photometer was calibrated for specific solutions such as boiler condensates and softened waters but not for natural waters. A follow-up with Palintest did not resolve the issue in time for the last round of testing.

Precision

Precision is a measurement of repeatability of a result under unchanged conditions. For our data, an average value of at least three repeat photometer readings was calculated for each test along with the standard deviation of the data set. The precision of each test is reported as the average relative standard deviation (expressed as a %).

Overall, the photometer readings were found to be highly reproducible (Table 4), with the exception of the Mg and turbidity measurements. The poor precision reported for these measurements can be attributed to two main factors:

1. The first factor is the occurrence of outliers. For example: repeat turbidity measurements record results of 2, 2, and 4 (Formazin Turbidity Unit: FTU), for a relative standard deviation of 43% (a lower percentage represents a higher precision). For Mg, repeat measurements record 4, 1, and 0 ppm, for a relative standard deviation of 125%. The tests for Cl^-, SO_4 and SiO_2 occasionally exhibited this behaviour but these instances were not numerous enough to affect the overall level of precision. This issue has been brought to the attention of Palintest and we are working collaboratively to resolve the issue.
2. The second factor contributing to lower precision is the low concentration of Mg and the low turbidity values in most samples, with values that are very close to the detection limits (values registered as "Below Detection" were not used in the calculation of precision). For example, three repeat Mg readings of 1, 0, and 0 ppm yield a relative standard deviation of 141.42%. When concentrations are elevated however (e.g., Turbid Creek), relative precision improves due to division by a larger value (Mg at Turbid = 1.20 % relative standard deviation).

In contrast, despite the issues described earlier for Cl^- and SO_4, their overall precision was respectable (24% and 6%, respectively). SiO_2 measurements have an excellent precision with a relative standard deviation of 2.41%.

The lower precision of the various tests at low concentrations is not considered an issue because the survey methodology aims to identify anomalous concentrations that are well above background values, and hence, largely above the detection limit of the instrument (see the "Background levels and threshold values" section).

Accuracy

Accuracy is a measurement of how close a value is to the "true" value. In our case we considered the ALS lab value as the true value. We established the following ranking system: 0-10% relative error = excellent agreement with lab results (i.e. excellent accuracy); 15-30% rel. error = acceptable agreement/accuracy; > 30% rel. error = poor/unacceptable.

Despite minimizing the procedure error for SO_4 during the last round of tests, overall accuracy is still poor, with a relative error of 623.75% (Table 4). Concerns have been conveyed to Palintest and the issue is currently under investigation. If the data offset is consistent, this offset can be corrected for. Despite the elevated relative error on the SO_4 readings, anomalously mineralized waters are still discernible above the elevated background noise levels (see below).

For Mg, most of the concentrations measured, with the exception of Turbid Creek, are close to or below detection limit, therefore relative errors are large (Table 4). As with precision, accuracy improves for samples with elevated concentrations of solutes. Such is the case for Turbid Creek, which has an accuracy of 23.57% for Mg.

Background Levels and Threshold Values

In order to identify mineralized surface waters, the regional background level for each species was determined. Cumulative probability graphs were constructed for each species, for each season, using the complete regional data set. An example from SiO_2 is shown in Figure 3. The SiO_2 data has a log normal distribution and shows one principal inflection point on the cumulative

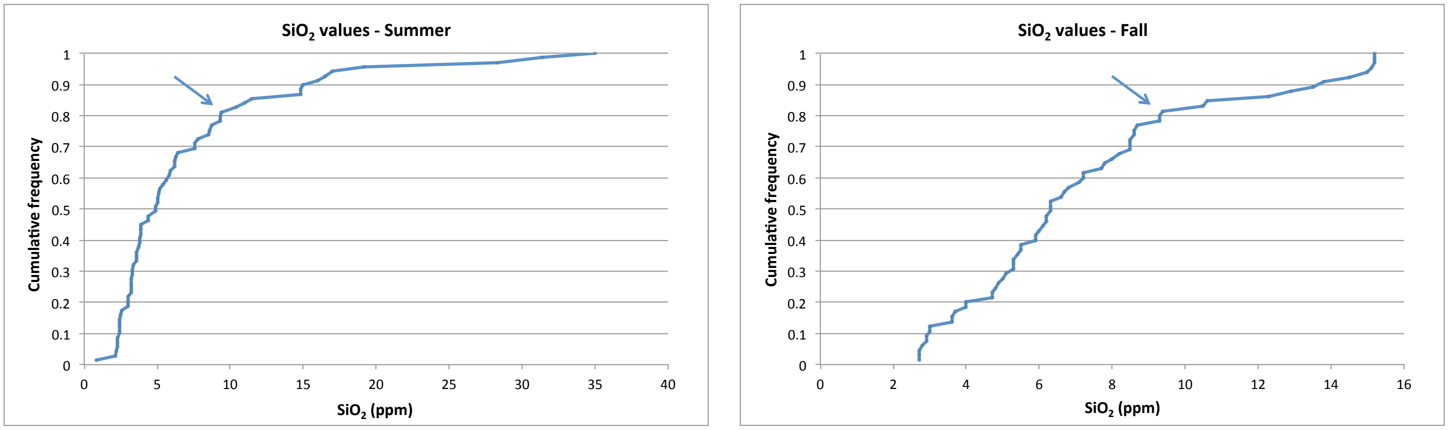

Figure 3. Cumulative frequency plots for SiO_2 values in both the summer and fall seasons. The main inflection point occurs around 9 ppm in both graphs and is considered the upper bound of background values.

frequency graph for both seasons at ~9 ppm. We interpret this inflection point as representing the upper bound of background level SiO_2 concentrations and we consider any sample with > 9 ppm to be anomalous. For SO_4, the large amount of noise in the photometer data means the background threshold level is high and values above 25 ppm, regardless of the season, are considered anomalous. For Cl^-, values above 2 ppm are considered anomalous, again regardless of the season. Although Mg is not generally enriched in geothermal waters, Ryder (1983) found elevated concentrations in the waters downstream from the hot springs at Mount Cayley. The hot springs themselves were found to contain 168 ppm Mg at Turbid and 13 ppm at Shovelnose (Dellechaie, 1984). We found that the background threshold concentration for Mg is 2 ppm, regardless of the season.

Discussion

The photometer results for each chemical species are compared amongst the creeks in order to identify relative anomalies (Figure 4). Additionally, the photometer chemistry results for

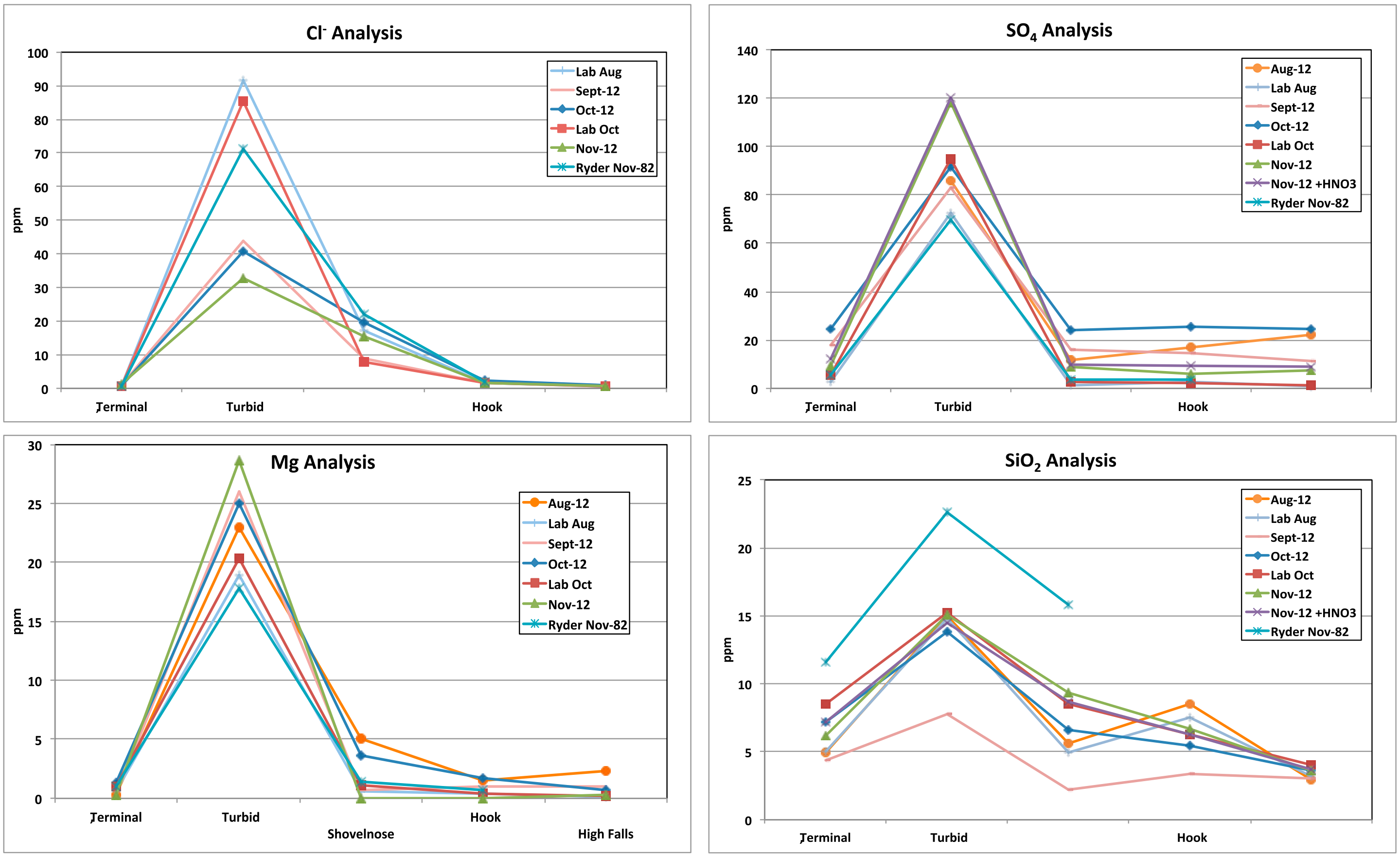

Figure 4. Analysis of individual ionic signatures across creeks and their seasonal comparison.

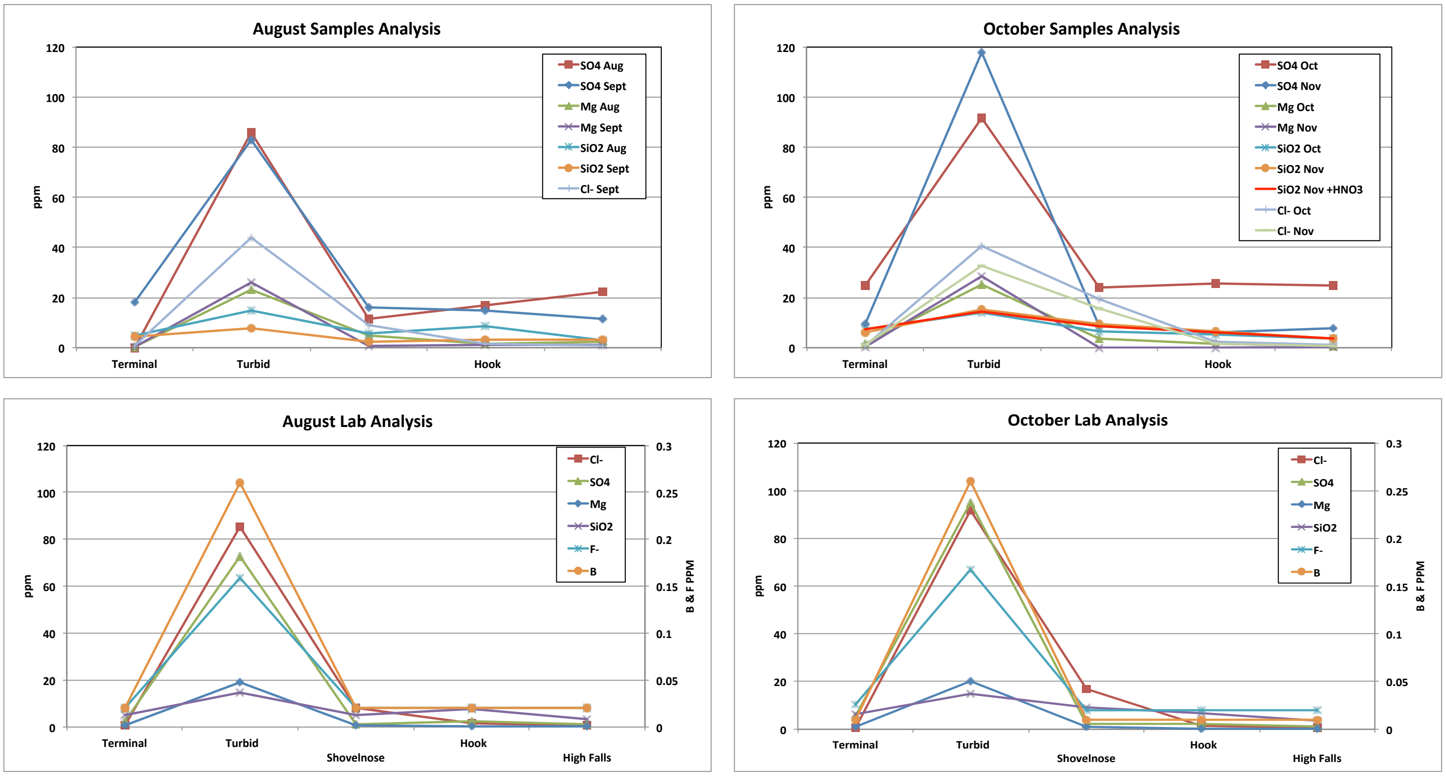

Figure 5. Summer and fall chemistry across the creeks compared to the corresponding lab analysis.

both seasons are compared with the lab results (Figure 5). When displaying the lab results, boron (B) and fluoride (F^-) are included as additional geothermal indicators (Figure 5). Their correlation with Cl^- and SO_4 suggests they could be used as indicators during future surveys.

Both Turbid and Shovelnose Creek have Cl^- concentrations above background levels (> 2 ppm) and show a distinct relative enrichment compared to the other creeks (Figure 4). However only Turbid Creek has elevated SO_4, SiO_2 and Mg concentrations as well, and this signature is present in both the summer and fall samples. The Cl^- anomaly at Shovelnose Creek mirrors its hot spring composition (chloride-rich water) and the Cl^- and SO_4 anomaly at Turbid Creek matches its hot spring composition (chloride-sulfate water). Interestingly, the SiO_2 and Mg anomaly recorded downstream along Turbid Creek is not duplicated at Shovelnose Creek despite elevated concentration of both species in the hot springs. In fact, SiO_2 concentrations downstream at Shovelnose Creek are only slightly above background in the fall samples (average of ~8 ppm from photometer and laboratory results) and Mg concentrations are within background levels (average 1 ppm). The relative concentration of species at each creek measured in 2012 compares well with Ryder's results.

For the other creeks, all analyzed species concentrations are within background range with the exception of SiO_2, which is slightly elevated above background at both Terminal and Hook Creek (average of 7 ppm in the fall sample of Terminal Creek and average of 6 ppm at Hook Creek). In comparison, Ryder (1983) had emphasized a slight SO_4 anomaly at both these creeks, despite also reporting a small SiO_2 anomaly (~12 ppm SiO_2). Based on our results only, the lack of a coinciding Cl^- or SO_4 anomaly at these creeks precludes us from attributing these SiO_2 concentrations to a geothermal anomaly upstream.

Only a small seasonal variation was identified when comparing results from the summer and fall campaigns (Figure 5); in most cases absolute species concentrations are slightly higher in the fall. This small variation is attributed in part to the large amount of rainfall (40-50 mm) that fell before the fall sampling took place. In fact, there is no clear pattern for the creek water levels between the two seasons: Turbid and Hook Creek have higher discharge rates in the fall but Shovelnose, Terminal and High Falls recorded lower discharges in the fall compared to the summer.

Conclusions and Recommendations

The goal of this pilot survey was to investigate the accuracy and precision of the Photometer 8000 for chemical analysis of creek waters, with the end goal being to use the photometer to detect anomalous concentrations of geothermal indicators in dilute surface waters and locate upstream thermal sources. The photometer demonstrated that it is an excellent tool for delivering results in real-time. Further tests should be conducted to improve the analysis technique and refine the survey methodology, with the goal of improving the accuracy and precision of the data and increasing the signal/noise ratio.

The photometer has the potential to reduce grass roots exploration costs considerably. The ability to determine the composition of thermal waters in the field is an immense advantage for an exploration company looking to perform either a limited, but detailed survey, or an extensive reconnaissance field campaign. This technique would be valuable in humid jungle regions such as the southwest pacific region, where many of the world's largest geothermal systems are found, and where remoteness makes it likely that many surface geothermal discharges remain undetected. Additionally, the photometer could be used as a mobile lab for analyzing drilling fluids. The ability to acquire fluid compositions on site might aid in the real-time decision making required for such expensive operations.

Based on the pilot test, it is recommended that boron and fluoride be incorporated as two additional geothermal indicators. Testing for five indicators (Cl^-, SO_4, SiO_2, F^-, B) is more rigorous and could provide more conclusive results. The cost for each reagent is negligible at $1 US/tablet except for boron where the cost per reagent tablet is about $2 US.

To ensure the most accurate results, photometer analyses should be conducted within 24 to 48 hours. This eliminates the need to preserve silica using HNO_3 and reduces the amount of sample to be collected and processed.

Any turbidity variations present (post filtering) were found to have no effect on the results. This test does not need to be conducted during future surveys.

Although a reagent is available to test for potassium (K), unfortunately no free sodium (Na) and calcium (Ca) tests are available, which would have allowed us to obtain real-time cation geothermometry estimates for thermal waters, in addition to the Si geothermometry. Discussions are underway with Palintest to find solutions to enable us to obtain estimates of Na and Ca.

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