



**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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Executive Summary

Building on the successful outcome of a 2014 Geoscience BC project ([Report 2015-17](#)) this project aims to add to the wealth of data available in the TREK project area. It extends the real-time hydrogeochemical-survey methodology to a regional setting while at the same time investigating the effects of seasonal variation. Stream water samples were collected and analysed in an area immediately southwest of Nazko, BC. Underlying bedrock consists of widespread Tertiary basalts (Endako Group) overlying older volcanic and sedimentary rocks belonging to the early to middle Cretaceous Skeena Group and middle to late Jurassic Hazelton Group. One hundred and fifty-five water samples were collected and analyzed at Nazko during sampling campaigns in June, August and October 2016. A suite of cations and anions was analysed for by portable photometer and electrochemical voltammeter. Nineteen samples were also sent to an ALS Environmental laboratory in Burnaby, BC for cations and anions analysis. Considering the above average precipitation during the field season, results still provide a good understanding of how the analyte responds to seasonal variations. Results show a good correlation between field and laboratory analyses with acceptable levels of accuracy and precision. Anomalous values for Cu and As were detected in streams draining two known mineral occurrences.

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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), and environmental (Saha and Sahu, 2015). Building on the successful outcome of Geoscience BC Report 2015-17 (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 aimed to extend the real-time hydrogeochemical survey methodology to a regional setting, while at the same time investigating the effects of seasonal variations, and the potential for rapid, field-based detection of anomalous hydrogeochemically detectable 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; Lonsdale and Wajrak, 2013), an electrochemical method based on anodic stripping voltammetry (ASV). A small orientation survey was performed in the Lower Mainland to determine optimum sampling procedures.

Study Objectives

The aim of sampling in the Nazko area (Figure 1) was to determine if rapid hydrogeochemistry surveys will work in a hydrologically complex environment. In addition, the study area was chosen because of interest from the Nazko Economic Development Corporation in assessing potential for resource-based economic development.

Photometer technology and field data collection methodology is discussed in detail in GBC Report 2015-17 (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 map sheet area (NTS 093B13).
- Investigate seasonal variability of water chemistry by repeating the sampling campaign in spring, summer and fall.
- Investigate the hydrogeochemical expression of known mineral occurrences in the area.
- 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 PDV6000*Ultra* voltammeter for rapid hydrogeochemical surveys.

Location and Access

The study area is located south of Nazko (Figure 1) and approximately 75 km west of Quesnel in central British Columbia (Marmot Lake map sheet, 093B/13). Two mineral showings occur in the area and

provide a focus for the regional-scale sampling. Furthermore, water geochemical data from recent sampling in the project area are available for comparison (Lett and Jackaman, 2015).

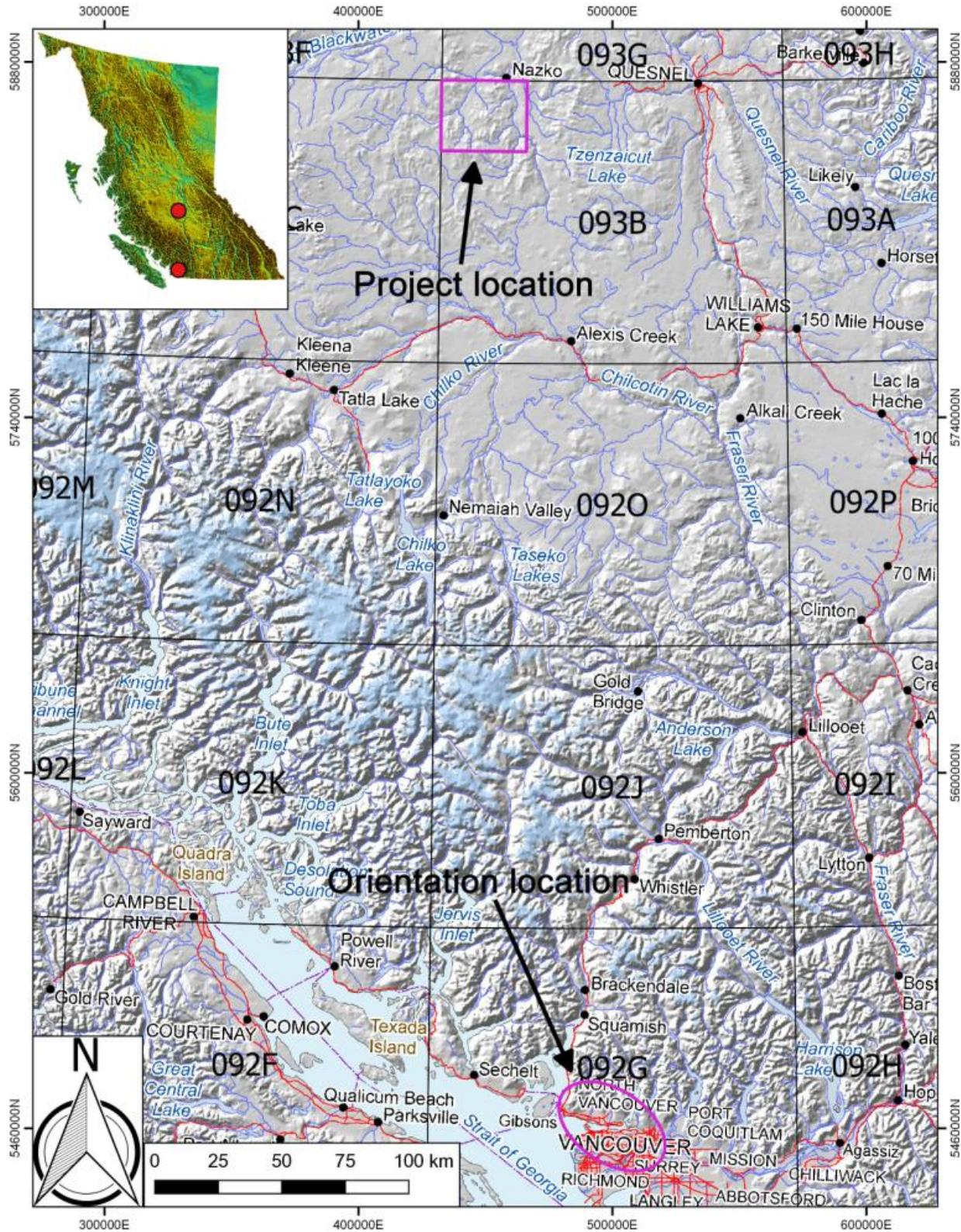


Figure 1. Location map.

Access is via the paved Nazko Road (HW 59) and an extensive system of forestry roads (Figure 4). Elevations range from 850 to 1250 m above mean sea level. Accommodation and logistical staging was from the Blackwater logging camp, which was made available as in-kind support from the Nazko Economic Development Corporation (NEDC).

Geology

Study area geology is characterized by widespread volcanic and sedimentary rocks of different ages (Figure 2). Older volcanic and sedimentary rocks include the Miocene to Pliocene Chilcotin Group basalts along the east-side of the Nazko River. The youngest rocks exposed in the survey area are basalts of the Miocene to Holocene Anahim volcanic belt (Unit HoA), the easternmost limit of which is represented by the Nazko volcanic cone that erupted approximately 7200 years ago (Cassidy et al., 2011). Underlying the Chilcotin Group (Units MiCB and MiCl; Figure 2) are volcanic rocks of the Eocene Ootsa Lake Group (Unit Vd), which are the most widely exposed. Volcanic and sedimentary rocks of the Lower to Middle Jurassic Hazelton Group (Unit LMJH) occur in the northeast corner of the study area (Massey et al., 2015). The Hazelton volcanic sequence consists mainly of andesitic and basaltic flows, and lesser amounts of pyroclastic rocks. 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.

In addition to the Nazko industrial mineral deposit (lava rock), there are two sulphide mineral occurrences in the project area: Fishpot, (BC MINFILE 093B066 - Au, Ag, Cu, As, Ba and Sb) in the northwest; and Bob, (BC MINFILE 093B 054 - Au, Ag, As, Sb and, Hg) located just south of Nazko and east of the Nazko volcanic cone.

Copper-As-Au mineralization at Fishpot is hosted in an Eocene-age pyritic quartz rhyolite porphyry plug that intrudes Late Jurassic Hazelton Group pebble conglomerate, shale and tuffaceous sandstone. Two styles of alteration identified on the prospect consist of carbonate-limonite staining (after pyrite) and limited quartz veining (Kennedy, 2012).

The Bob prospect, which has been more thoroughly explored, is underlain by Lower Cretaceous to Lower 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 rocks. Anomalous Au, As, Ag, Sb and Hg levels have been reported from Skeena Group rocks from areas that have undergone silicification and argillic alteration and contain carbonate minerals and pyrite.

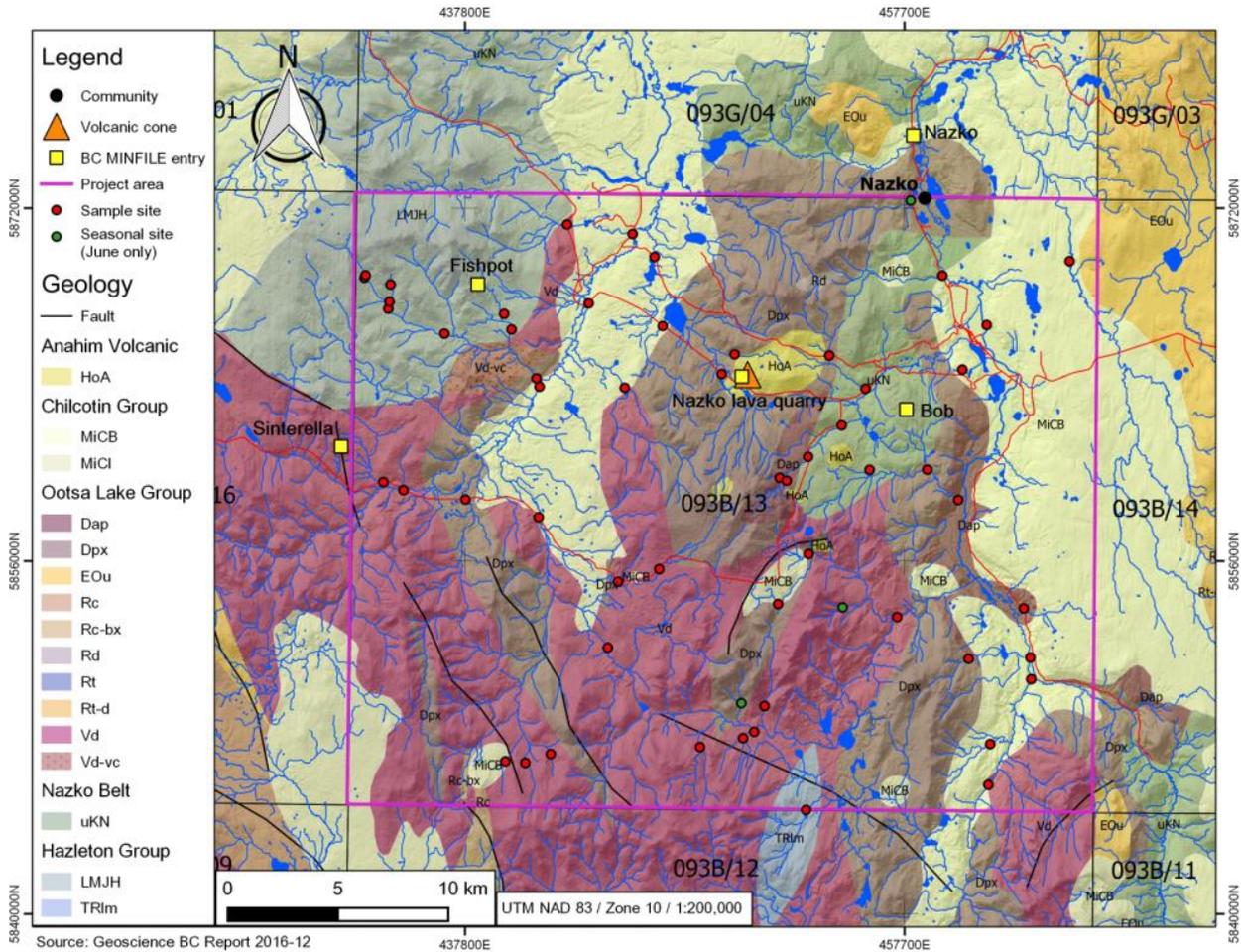


Figure 2. Local geology of study area (Bordet and Hart, 2016).

Surface Environment

The area has an abundance of glacial deposits of various thicknesses. Till is the most widespread surficial deposit. It covers bedrock over large parts of the map area. The most recent ice-flow direction is from the south-southwest. Sacco et al. (2014) demonstrated that much of the region is covered by a basal till veneer (<2 m) or a thicker basal till blanket (>2 m). Fluting and drumlin-like landforms are visible as streamlined surface features formed by moulding of the glacial sediment by the advancing ice. Undulating and hummocky ablation till was deposited from stagnant ice-captured englacial and supraglacial sediment in lowland areas and along valley margins. Bedrock is exposed locally on steeper slopes and along incised valleys. Poorly to well sorted sands and gravels that were deposited directly by glacial melt water produce glaciofluvial veneers, glaciofluvial blankets, ice contact deposits and eskers. Gravity deposited sediment on steeper hill slopes (colluvium) forms local colluvial fans, veneers and blankets. Fens, bogs, swamps and lakes have developed on alluvial sediments that fill creek valleys and melt water channels.

The north-flowing Nazko River traverses the eastern part of the area. Another large river, the Baezaeko, flows from southwest to northeast in the northwestern part. Lesser water courses defining a dendritic drainage pattern include small creeks, lakes and wetlands. Some of the water courses have alterative creek and wetland morphology; the wetlands are often caused by beaver activity. The forest canopy is dominated by lodgepole pine (*pinus contorta*) and many of the trees have been severely damaged by the mountain pine beetle infestation. This infestation has increased tree harvesting and, consequently, has improved road access throughout the project area.

Field Conditions

Average June precipitation in 2014 and 2015 was 47.6 mm and 31.4 mm respectively (recorded at the nearest Environment Canada weather station in Quesnel). June 2016 proved to be wetter with a total of 68.1 mm of precipitation recorded in Quesnel. July was wetter than normal with over 82 mm of rain falling over the region (Figure 3). Thus, the first sampling campaign was carried out under abnormally wet conditions which caused an increase in water turbidity. Many creeks overflowed their banks before and during the sampling campaign.

The wet conditions complicated vehicle access by creating impenetrable mud on many secondary logging roads; foot access was complicated by high water levels in creeks and wetlands. The adverse conditions made sampling at some stations and subsequent follow-up quite challenging. Conditions were drier in August, but water levels remained high due to continued precipitation in July. Nevertheless, road and foot access was markedly improved from the June campaign.

Field work in October was also challenging because of higher than normal precipitation. This caused many creek levels to rise and further increased the water turbidity. Throughout October, heavy rain showers created unpredictable water levels, which unlike June and August varied across the study area. Adverse conditions were compounded by snowfall, heavy at times, during the later stages of the field work. Sample collection had to be accelerated in anticipation of loss of access to some areas due to accumulations of snow.

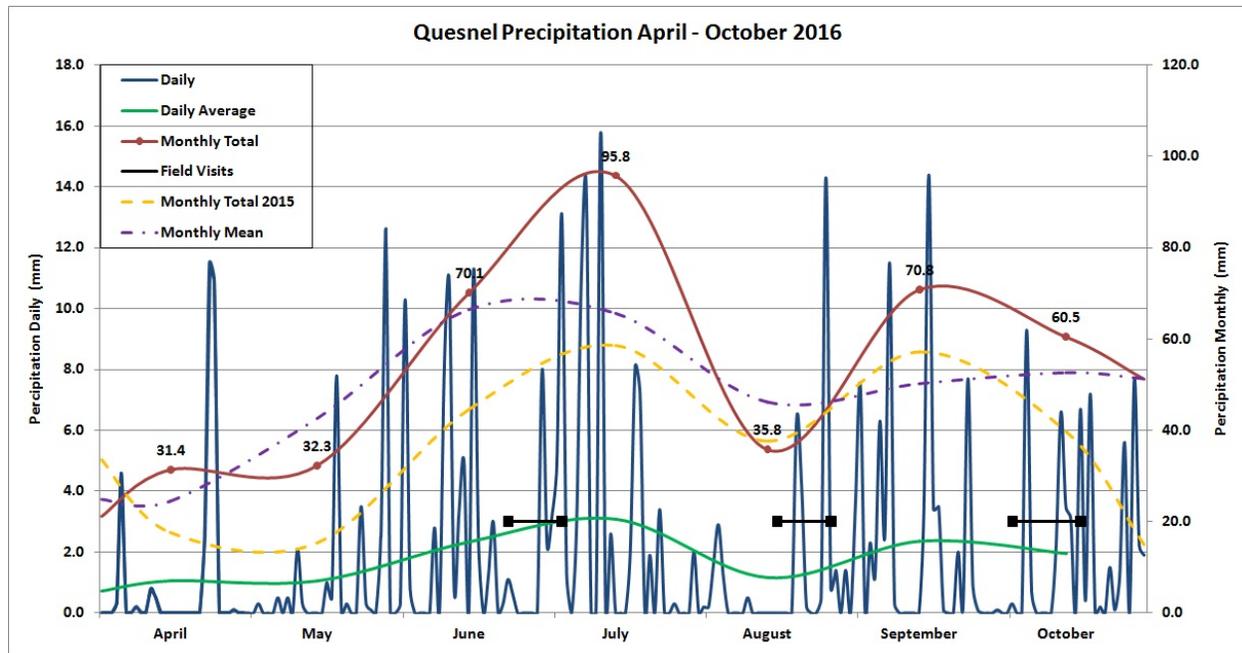


Figure 3. Precipitation for Quesnel at the time of the sampling campaign (Environment Canada, 2016).

Sample Collection

Orientation Survey

One of the recommendations in Yehia and Heberlein (2015) was to carry out a small orientation survey prior to the field surveys. It was designed to optimize sampling, sample preservation (Hall, 1998; Khanna et al., 2009) and analytical methods for the Palintest® Photometer 8000 and the PDV instrument. Water sampling was carried out at three locations in the Lower Mainland: 1) at Furry Creek and Britannia Creek, which drain the Britannia mine area; 2) at Lynn Creek in the Lynn Headwaters Regional Park; and 3) from a creek flowing southwest of Fraserview Golf Course in Vancouver. The sample stations were chosen for: 1) ease of access for testing sampling methods during the spring runoff, 2) testing the ability of the field-based methods to detect elements of interest in the stream water, and 3) comparing results of laboratory and field-based water analyses. Four water samples were collected 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), a set of unfiltered and acidified samples were sent to the ALS Environmental laboratory (Burnaby, BC) for comparative analysis. Unfortunately, the PDV instrument was unavailable for the orientation survey.

Study Area

Stations were selected based on the presence of active drainages as close as possible to existing TREK and QUEST sample locations, previously unsampled stream catchments and access. The number of sites sampled around the Bob and Fishpot mineral occurrences was lower than initially planned (Figure 4) due

to a lack of suitable creeks draining the Bob prospect and the presence of dry glacial outwash channels around the Fishpot showing that were not recognized during project planning.

In subsequent campaigns, sampling was done around both occurrences, as well as regionally over the broader project area. Sample stations for the latter were chosen for their accessibility from the primary logging roads.

Table 1 summarizes the samples collected during the field campaigns. Water samples were mostly collected from the middle stream channels. A sampling device consisting of a water bottle holder attached to a 2.5 metre pole was used to collect a water sample where streams were too wide or the bank unsafe for manual sampling from the bank. Samples were collected in two sizes of #2 high-density polyethylene (HDPE) bottles: non-acidified samples in one litre bottles and acidified samples (with 3 ml ultrapure nitric acid) in 250 ml bottles. Neither sample was filtered in the field. Sample bottles were reused and rinsed thoroughly with the cap on three times with the water to be sampled before sample collection. After collection, samples were transported in a cooler and stored in a refrigerator at the camp before analysis.

Photometer and PDV analysis of the water samples was carried out usually within 24 hours of collection. Water temperature, pH, conductivity, total dissolved solids (TDS) and salinity were measured at each sample location using an Oakton PCS Testr 35 meter. These parameters were measured again as a quality-control procedure with a second PCS Testr before photometer and PDV analysis to prevent sample mix-ups and to monitor any changes in the sample chemistry after collection. Both meters were calibrated weekly. Differences in the pH recorded by the two instruments are in the order of 0.5 units.

In addition to measurements taken at each site with the Oakton meter, a variety of observations were recorded and are listed in the field observation spreadsheet included in the digital appendix. These included sediment and bank characteristics and water observations such as colour and hydrological volume; ranges listed from very small (less than one litre per second, <1/l), to large (100-1,000/l).

Table 1. Sampling completed in 2016.

Type	Sampled and tested	Laboratory samples
Orientation survey	4 sample stations (16 tests)	4
	1 deionized	
	1 SLRS-6 Standard	
June field survey	49 sample stations	8
	3 deionized	
	3 SLRS-6 Standard	
	3 analytical duplicates	
	3 field duplicates	
August field survey	50 sample stations	5
	3 deionized	
	3 SLRS-6 Standard	
	3 analytical duplicates	
	3 field duplicates	
October field survey	56 sample stations	6
	3 deionized	
	3 SLRS-6 Standard	
	3 analytical duplicates	
	3 field duplicates	
Total	208	23

At every tenth site a water sample was filtered through a 0.45 µm filter, acidified with 3 ml of 6M HNO₃ and sent to ALS Environmental laboratory in Burnaby, BC for multi-element analysis. Water in the 250 ml bottles was used for cations analysis, while the one litre sample was required by the laboratory for TDS, conductivity, turbidity, and anion determinations as well as for quality-control monitoring and reanalysis (if required). Water samples for laboratory analysis were transported in coolers to the ALS Environmental laboratory by the lead author the day after returning from the field. Laboratory determinations were for dissolved solutes, since both photometer and PDV measure the dissolved component by chemical interactions in the water sample.

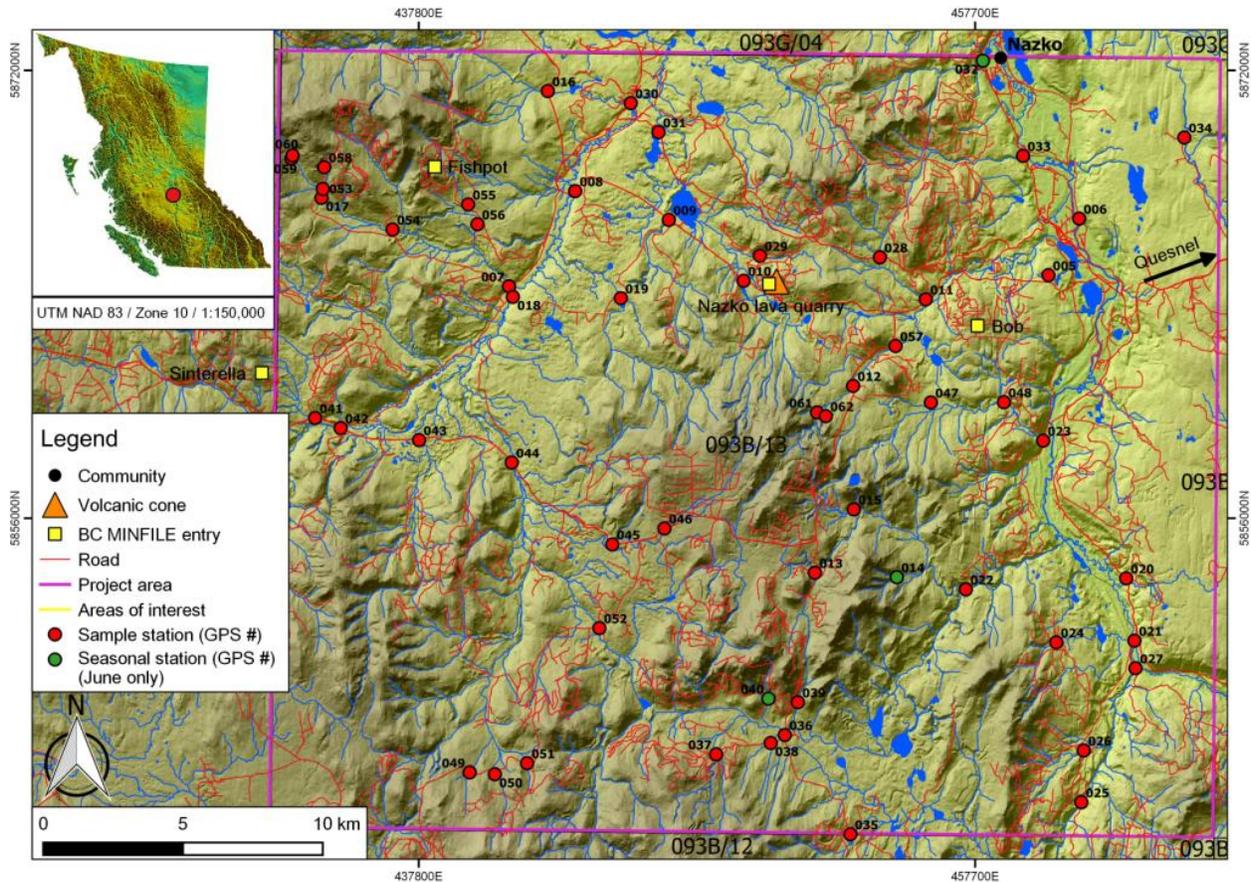


Figure 4. Map showing location stations with GPS waypoint number.

Quality Control Measures

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 (second bottle from the same sample station).
 - 1 analytical duplicate (second test from same sample bottle)
 - 1 government-certified standard (NRC-CNRC SLR-6, certified river water for metal traces and other constituents)
 - 1 blank using ultrapure deionized water (18 MΩ)
 - 1 laboratory check for every tenth sample.

Analytical Methods

The photometer measures the absorbance and transmittance of metal-colour complexes at different wave lengths (e.g. 500 nm) to determine element concentration. The PDV uses anodic stripping voltammetry (ASV) to measure the ionic concentration of metals such as Cu, As, Pb, Cd in water (more below).

Portable devices can measure element concentrations to low detection limits suitable for geochemical exploration applications. For some tests, the photometer is capable of single digit micrograms per litre ($\mu\text{g/l}$, or ppb) levels, while the PDV can achieve slightly lower detection limits for some analytes. While some of the cation tests are not as sensitive as laboratory methods (Table 2), the detection limits are low enough to reliably measure meaningful geochemical variations in the field.

Table 2 summarizes the performed analyses and the detection limits for both devices.

Table 2. Tests performed by the portable devices chosen for this project.

Type	Photometer detection limit (mg/l)	PDV detection limit in clean water (mg/l)	Laboratory detection limit (mg/l)
Aluminum (Al) ¹	0.005		0.0010
Arsenic (As)		0.0005	0.00010
Cadmium (Cd)		0.0005	0.0000050
Calcium hardness	0.5		1.0
Chloride (Cl ⁻)	0.05		0.50
Copper (Cu, ionic and total)	0.005	0.0005	0.00020
Fluoride (F ⁻)	0.005		0.020
Hardness	0.5		0.50
Iron (Fe) ¹	0.005		0.010
Lead (Pb)		0.0005	0.000050
Magnesium (Mg) ¹	0.5		0.10
Manganese (Mn)	0.0005		0.00010
Molybdate (MoO ₄)	0.005		(Mo) 0.000050
Nickel (Ni)	0.005		0.00050
Potassium (K)	0.05		0.050
Silica (High Range, SiO ₂)	0.05		5.0
Sulphate (SO ₄)	0.5		0.30
Zinc (Zn)	0.005		0.0010

¹Photometer reagent that can be used with nitric acid preservation.

Tests for both devices in Table 2 are for dissolved constituents except for the Cu total test, which also includes Cu adsorbed onto suspended particulates. The first part of the Cu test measures the concentration of dissolved (ionic) Cu species in the sample. The addition of a de-complexing agent to the sample liberates weakly bound Cu thereby allowing a measurement of total Cu concentration. This test has the advantage over the rest of the tests of allowing measurement of the total concentrations in the field which are generally higher than dissolved concentration.

Another test that requires explanation is the Zn test, which when Cu is present is actually a Zn + Cu test. The Zn determination uses the Zincon (pyrithione zinc) test in an alkaline solution. Copper reacts in similar fashion to Zn in the test, and Ethylenediaminetetraacetic acid (EDTA) tablets are needed to suppress the competitive Cu-Zincon reaction. In addition, the EDTA breaks down the Zn species colour complex by binding preferentially to Zn and cleaving the Zincon complex leading to a reduction in the total colour complex formed (Lendrem, Pers. Comm., 2016).

Photometer

As described in Yehia and Heberlein (2015), the primary portable analytical instrument used in the study was the Palintest® Photometer 8000 (Figure 5). The photometer determines ion concentrations by measuring the colour and light transmittance of a solution after the addition of metal-sensitive colour dyes; a technique called visible light reflectance photometry. This device can measure concentrations of a diverse suite of dissolved anions and cations to relatively low detection limits. Analytical procedures used for this study were identical to those described in that report with the main exception being that almost all the analyses for this project were completed on the same day as the sampling and not within 48 hours of collection as was the case for the previous study.



Figure 5. A typical set-up for photometer analysis. Reagents are in silver packaging aligned atop. Coloured sample solutions ready for analyses are shown in the 10 ml tubes in the rack. The Photometer is in the centre right of the photo.

Another procedural modification for photometer analysis was the introduction of additional steps to compensate for the high turbidity of many of the samples. The photometer uses a separate tube as a 'blank', against which all reagent tests are compared. In previous studies, the photometer tests used deionized water for the blank as turbidity was negligible. 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 (Lendrem, pers. comm., 2016). At 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 it 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 water as a blank counteracts the turbidity effect and maintains the FTU below 10 to promote more accurate results.

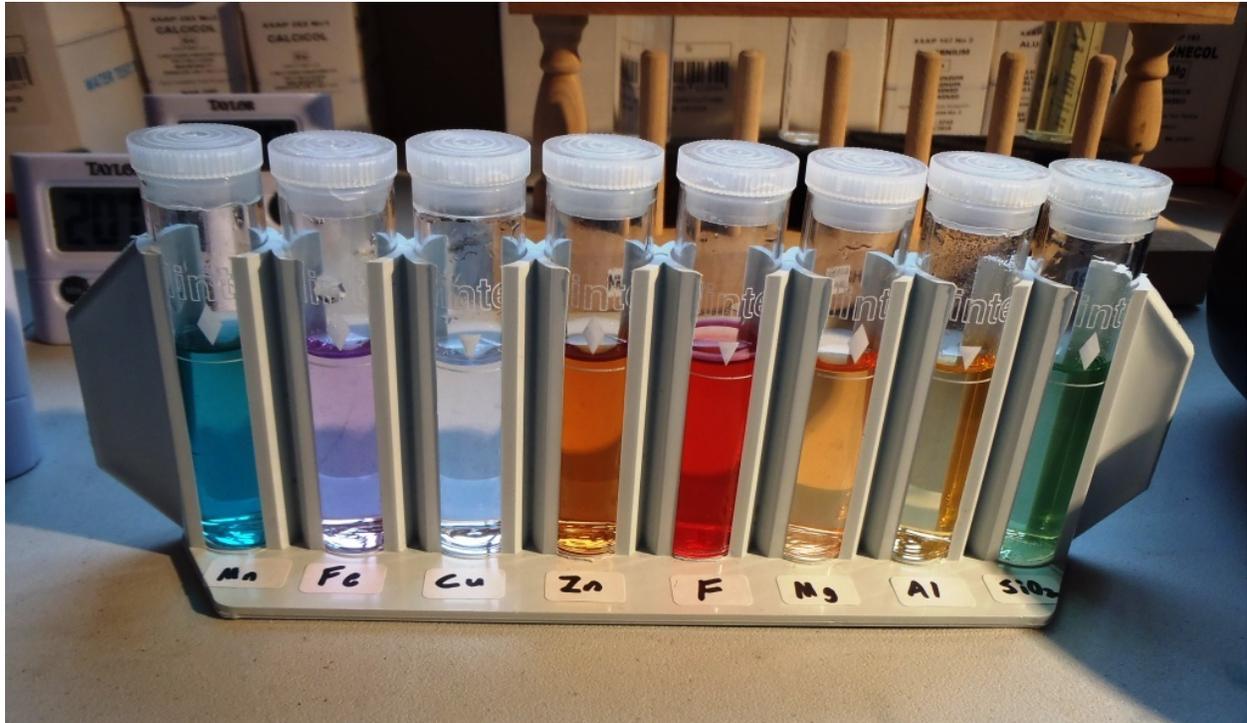


Figure 6. A collection of reagents ready for photometer testing. Note the clear Cu test (third from the left) that could be susceptible to turbidity interference, which occurs when the photometer records a false concentration because the solution is darker due to turbidity.

PDV6000Ultra

A second portable instrument, the Modern Water's PDV6000Ultra was used to increase the number of analytes measured (Figure 7). The instrument employs an electrochemical method based on anodic stripping voltammetry (ASV)(Baron-Jaimez et al., 2013). ASV involves applying a reducing potential over a time interval to electrodes. When enough metal has been coated onto the electrodes, the metal is stripped (oxidized) off the electrodes by increasing the potential at a constant rate. As the metal ions are released, a current is produced, which for each ionic species has a specific signature. This signature is then plotted on a "voltammogram" where the analyte concentration is displayed as a peak (Figure 8).



Figure 7. PDV set up used for this study. The PDV is resting on top of the yellow case, and the cell containing the test electrodes and the sample water reside in a holder just above the case handle.

For each testing day, the PDV was prepared using Modern Water's guidelines. Electrodes were examined and prepared in the testing cell. Blank and calibration runs were made until they were found to fall within a 5% margin (further examples in PDV Quality Control Results section). Figure 8 shows example voltammograms for a blank, a calibration standard and a Cu run. A set of five samples is analyzed at a time. After each group of five analyses, the electrodes are tested for any blank or calibration drift, and if needed, new blanks readings and calibrations are performed. If results are visually satisfactory, another set of five samples is run for a specific reagent test (i.e. As or Cd-Pb-Cu test).

Results are recorded both in Modern Water's Voltametric Analysis System (VAS) computer application, and manually on spreadsheets. Concentration values were noted using VAS's calculated peak height, and were verified as valid only when a peak was visually confirmed by an analyst.

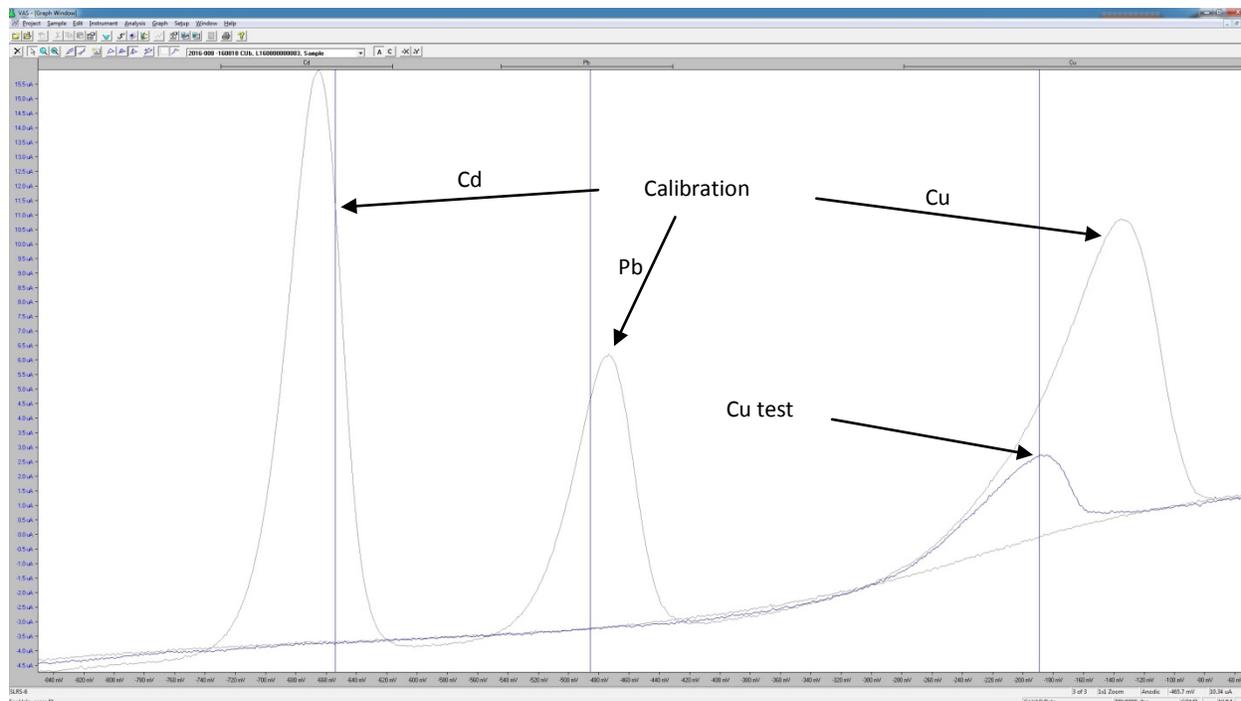


Figure 8. Example of a VAS plot for Cu sample, against a blank and three Cd-Pb-Cu calibration peaks. The X axis represents voltage in mV and the Y axis represents current in μA .

Health and Safety

Each reagent was accompanied by a Material Safety Data Sheet (MSDS). Members of the analytical team were required to wear nitrile disposable gloves and safety goggles. All solid waste associated with the study was disposed of in industrial-strength plastic garbage bags. Liquid waste, including used reagents and post-test rinse water were stored in a 22.7 litre (6 U.S. gallon) plastic pail with a special no-spill lid. All waste was taken to Terrapure's hazardous materials site in North Delta, BC for disposal.

Laboratory Analysis

Table 3 lists the analytical methods and protocols used by ALS Environmental on filtered water samples.

Table 3. Analytical methods employed by ALS Environmental¹

Type	Test	Test Description	ALS Test Code	Method Reference
Alkalinity	Titration	Total Alkalinity is determined by potentiometric titration to a 4.5 pH endpoint. Bicarbonate, carbonate and hydroxide alkalinity are calculated from phenolphthalein alkalinity and total alkalinity values.	ALK-TITR-VA ²	APHA 2320
Cl ⁻ , F ⁻ and SO ₄	Ion Chromatography		ANIONS-IC-VA	APHA 4110 B
Conductivity	[Automated]	Determined using a conductivity electrode	EC-PCT-VA	APHA 2510
Hg		Cold vapour atomic fluorescence spectrophotometry	HG-DIS-CVAFS-VA	EPA-245.7
Diss. Metals	CCMS & ICPOES	Procedures may involve preliminary sample treatment by acid digestion, using hot block or filtration. Instrumental analysis is by collision cell inductively coupled plasma – optical emission spectrophotometry.	MET-D-NDR-VA	APHA SW-846 3005A/6010B
pH	Meter [Automated]	Determined in the laboratory using a pH electrode.	PH-PCT-VA	APHA 4500-H
SiO ₂	Colourimetric analysis		SILICATE-COL-VA	APHA 4500-SiO ₂ E.
Total Dissolved Solids	Gravimetric	Determined by filtering a sample through a glass fibre filter. TDS is determined by evaporating to dryness at 180 degrees Celsius.	TDS-VA	APHA 2540 C
Turbidity	Meter	Determined by the nephelometric method.	TURBIDITY-VA	APHA 2130

¹ Cited from ALS reference information included with Certificate of Analysis

² VA - Laboratory Definition Code: ALS Environmental, Burnaby, British Columbia, Canada

QAQC

Photometer Accuracy

The photometer was monitored for drift using the manufacturer's standard dye solutions before each day's analysis. The standard colour solutions are traceable to standards BS 6376 and ISO 6353, and are supplied in sealed 10 ml tubes with expiry dates. The tubes are designated 38271/B (yellow), 38271/C (red) and 38271/D (green). Solution 38271/A is a clear solution (blank) that is used to reset the photometer before each test. Test values are in percent transmittance (%T) units. Results are charted in analytical order in Figure 9 to Figure 11.

The blank results demonstrate acceptable device accuracy. No test fell outside the manufacturer's recommended margin of error of ± 2 %T. For the green solution test shown in Figure 11, the reason for the difference between June's fluctuations and stable tests for August and October is unknown.

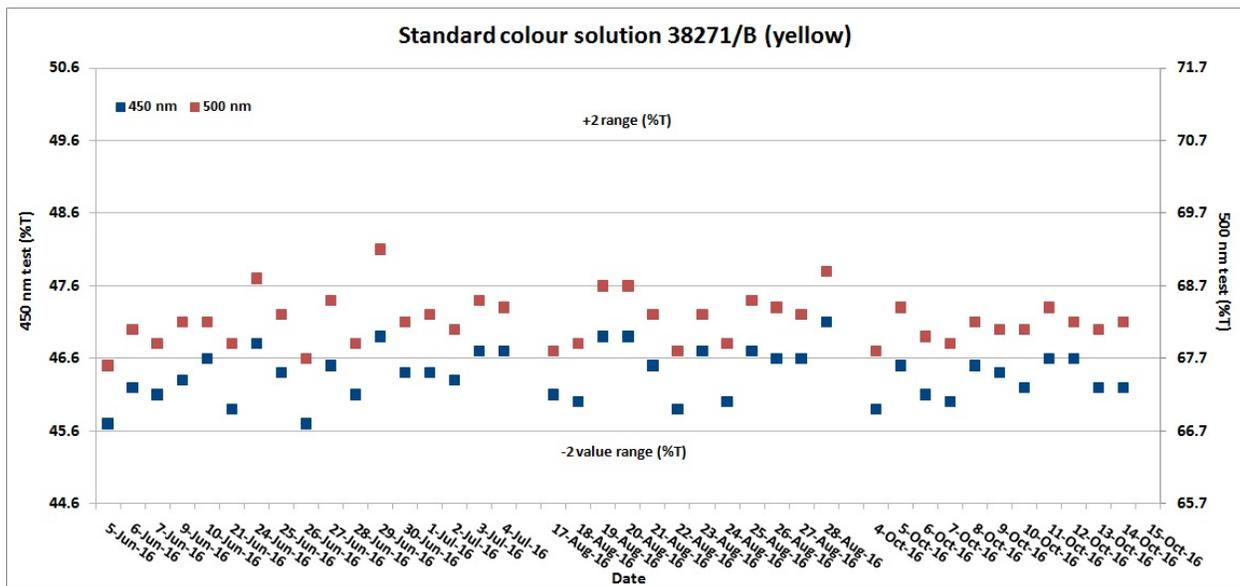


Figure 9. Control chart for standard solution 38271/B.

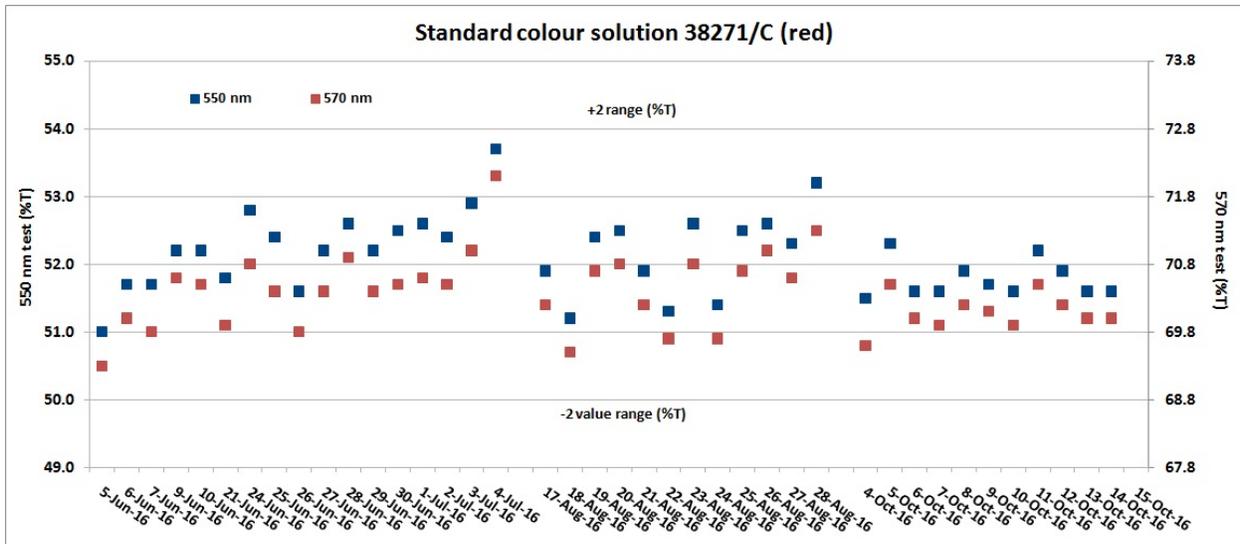


Figure 10. Control chart for standard solution 38271/C.

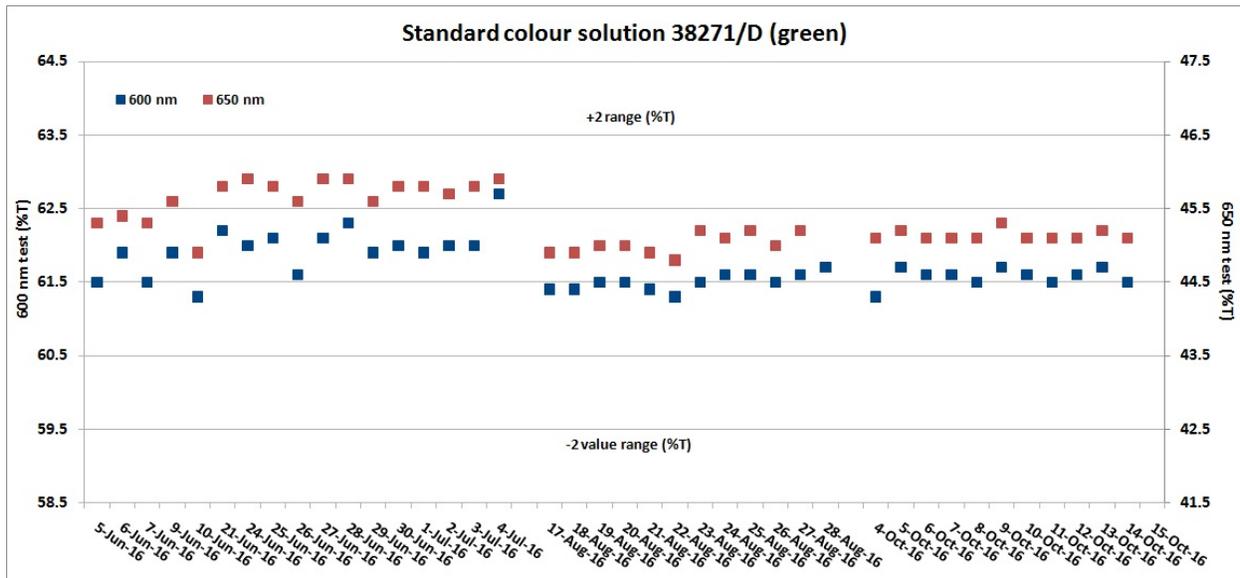


Figure 11. Control chart for standard solution 38271/D.

PDV Accuracy

For the PDV, accuracy tests are similar to those carried out for the photometer. For each reagent, a specific blank and a calibration standard is run before sample testing. At least three runs for each are performed and all must fall within a $\pm 5\%$ mV margin before proceeding to the sample determinations. Figure 13 show examples of Cd-Pb-Cu and As calibration runs.

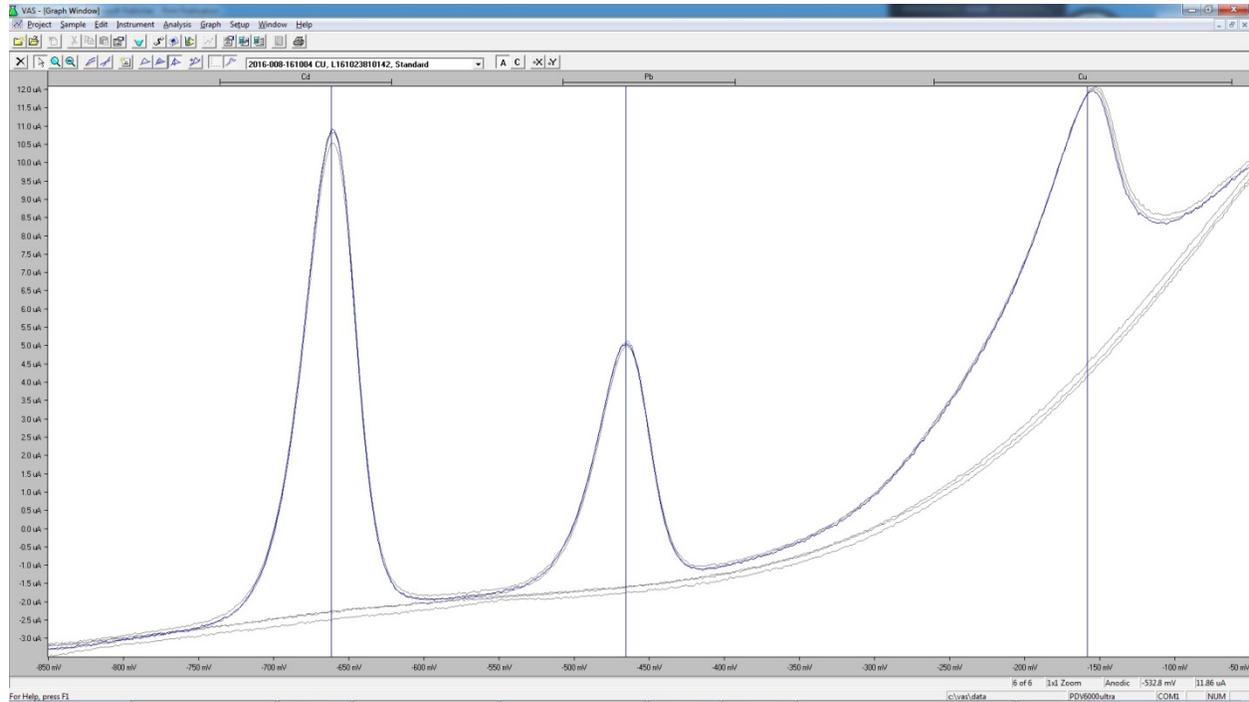


Figure 12. Example of a VAS plot showing Cd, Pb, and Cu standard calibration peaks ready for testing. Blanks are the flat profiles below the peaks. The X axis represents voltage in mV and the Y axis represents current in uA.

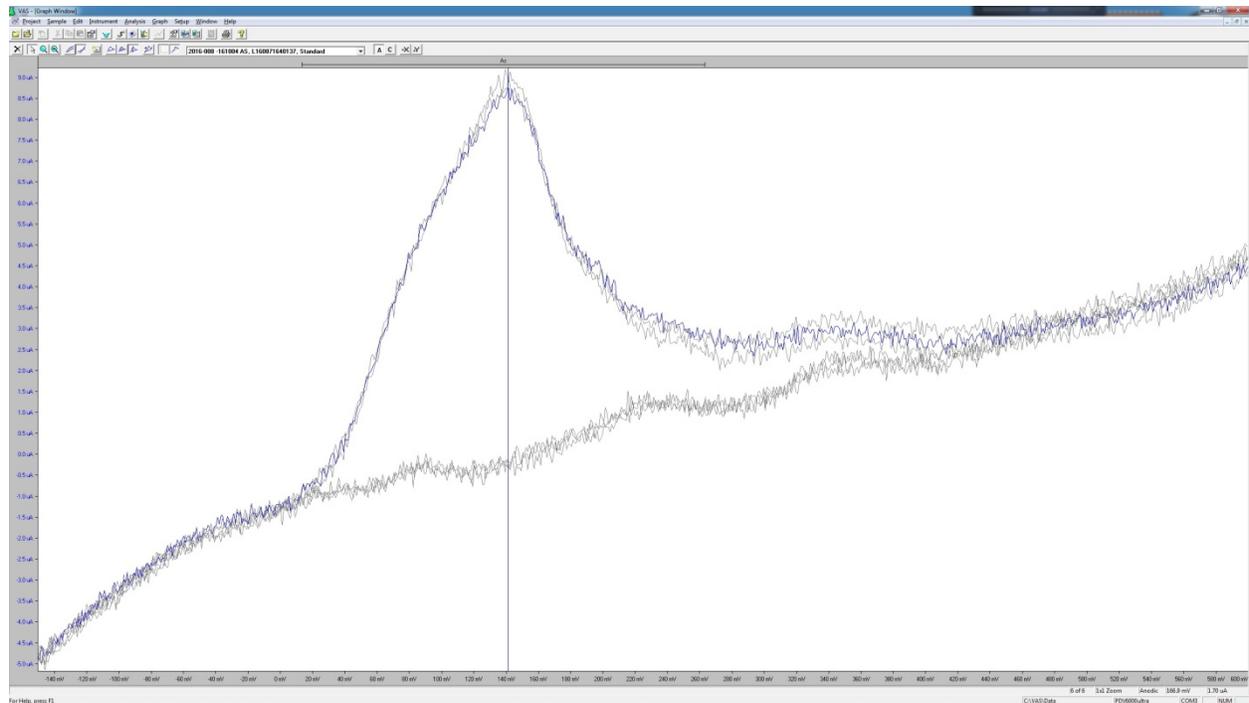


Figure 13. Example of an As standard calibration peaks ready for testing. Blanks runs are below the peaks. The X axis represents voltage in mV and the Y axis represents current in uA.

Photometer Precision

Assessment of the photometer precision, or measurement error, was done through triplicate analysis of the test solutions. Triplicate analyses provide an estimate of the precision of the analytical process. The process is described in detail in Yehia and Heberlein (2015).

For this study, precision is expressed as the average percent relative standard deviation or %RSD. It is calculated from the replicate and field duplicate results in a spreadsheet by first determining the mean and standard deviation of each triplicate or duplicate analysis and then calculating the %RSD value using the formula:

$$\%RSD = (\text{standard deviation}/\text{mean}) \times 100$$

Percent RSD results are then averaged for each analyte. Results for the photometer are presented in Figure 14. Precision is acceptable for most analytes, with all the reagents reporting %RSD values below 30% and almost all below 9%.

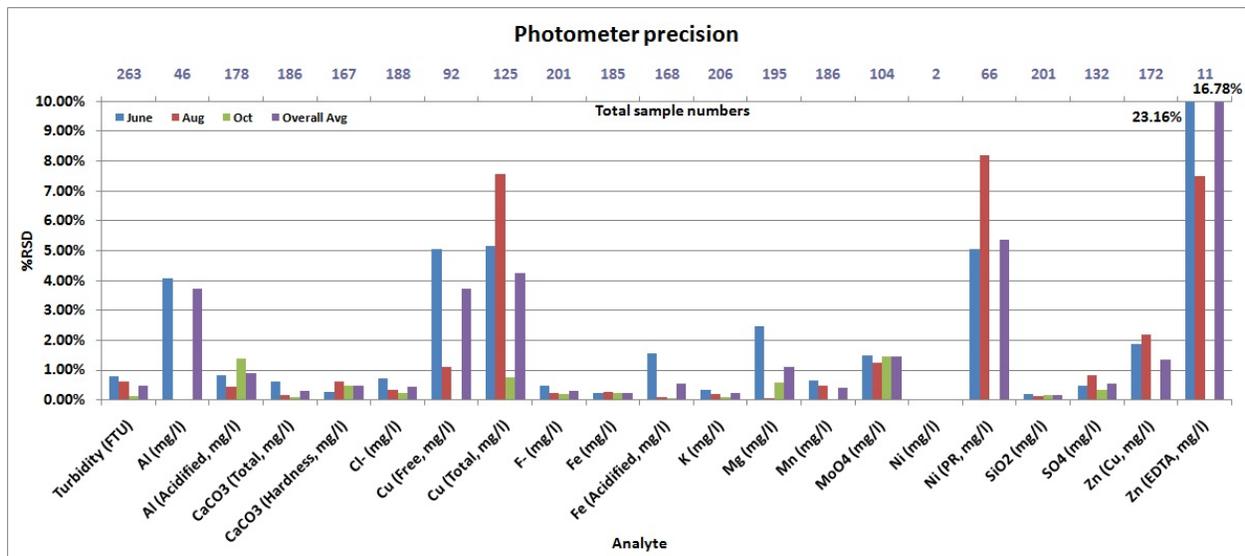


Figure 14. Percent RSD values estimated from photometer triplicate readings.

Field Duplicate Precision

Photometer precision (%RSD) calculated from the field duplicate results is presented in Table 4. Photometer duplicates analysis. Overall the results are well within acceptable precision levels (i.e. <30%). The best result is for Mn (0% RSD), while the poorest precision was for Cl⁻ for all three field visits.

Table 4. Photometer duplicates analysis.

Photometer analytical replicate data precision - %RSD													
Photometer analysis	Turbidity (clear, FTU)	Al (acidified, mg/l)	CaCO ₃ (Calcicol, mg/l)	CaCO ₃ (Hardicol, mg/l)	Cl ⁻ (mg/l)	F ⁻ (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Mn (mg/l)	SiO ₂ (mg/l)	SO ₄ (mg/l)	Zn (Cu, mg/l)
June													
June avg field dup	3.90%	18.75%	5.73%	7.11%	48.49%	6.92%	6.76%	3.05%	17.52%	0.00%	1.56%	3.84%	2.95%
June avg analytical dup	6.23%	16.13%	4.54%	14.11%	45.13%	7.82%	11.68%	0.54%	6.54%	0.00%	1.93%	8.32%	31.43%
August													
Aug avg field dup	4.55%	47.39%	15.70%	9.51%	20.27%	3.93%	19.72%	5.89%	10.95%	0.00%	20.10%	19.08%	28.28%
Aug avg analytical dup	7.43%	17.49%	21.18%	9.20%	28.17%	10.76%	16.34%	13.23%	13.42%	0.00%	14.86%	55.09%	35.36%
October													
Oct avg field dup	6.51%	18.20%	15.65%	13.44%	9.43%	13.61%	8.43%	18.06%	19.15%	0.00%	5.74%	32.64%	18.86%
Oct avg analytical dup	5.61%	15.98%	1.05%	4.07%	41.70%	6.39%	5.38%	10.73%	10.59%	0.00%	1.20%	8.32%	4.16%

Notes: 1) Lower % is better 2) %RSD = (standard deviation/mean) x 100

PDV Precision

PDV precision is calculated from repeat analyses done for various reasons; for example; repeat tests or check analyses. This could produce artificially high precision estimates since there are more sources of error when analysis is done at different times. Precision for PDV was measured at 9.00% for As (6 tests), 9.94% for Cu (15 tests), and 3.82% for Pb (2 tests). As with the photometer, results are well within acceptable limits (<30% RSD).

For the PDV, field duplicate analyses resulted in only one duplicate analyte that provided data for precision estimation. It is the As test done on October for GPS point #017, and field duplicate RSD was calculated at 0.1% and analytical duplicate at 6.7%.

In conclusion, the field and analytical duplicate analyses for both instruments indicate that the results are of acceptably accuracy and precision and of good enough quality to produce meaningful interpretations.

Laboratory Comparison

Field results were compared with laboratory ICP-OES analyses. They show a high degree of correlation for some analytes. There are some exceptions where the correlation is weaker, but these tests still provide meaningful results. ALS results are available in the Digital Appendix.

At approximately every 10th field station, a second sample was collected for laboratory analysis. In some cases, testing was paired with field and analytical duplicates. Locations were selected at random in the June survey. For the August and October campaigns, some laboratory samples were selected based on proximity to mineral showings, analyte concentrations or from the hydrogeochemical base station (more below).

Charts for Al (non-acidified), Cu (ionic and total) MoO₄, Ni, SO₄, Zn and Zn EDTA are not included due to insufficient data (above detection limit) available for meaningful interpretation.

Metals and Anions

Acceptable correlations between the field and laboratory analyses are shown for the CaCO_3 Hardicol (hardness), Ca, K, Mg, and SiO_2 results (Figure 15 to Figure 19). Hardness and K display the best overall correlation. There is some photometer high bias for hardness in June and slight high bias for K and Mg in June and August. Calcium (Figure 16) displays a good correlation but has a notable laboratory high bias. Calcium concentrations are converted by multiplying Calcicol (CaCO_3) results by 0.4. Despite having a photometer bias, SiO_2 results appear to show a reasonable correlation. The greatest bias between laboratory and photometer is present in the June results, but this may be explained by the higher turbidity levels at that time. As well, SiO_2 has the narrowest concentration range of the analytes tested (20-50 mg/l).

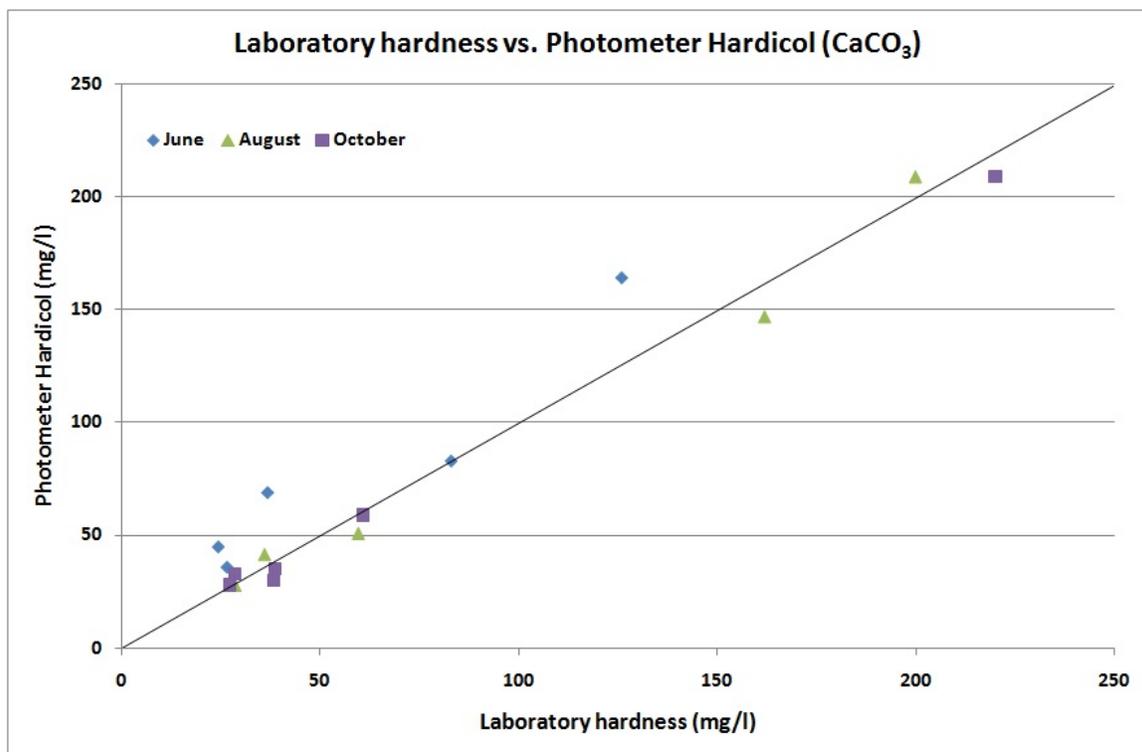


Figure 15. Hardness by photometer and laboratory.

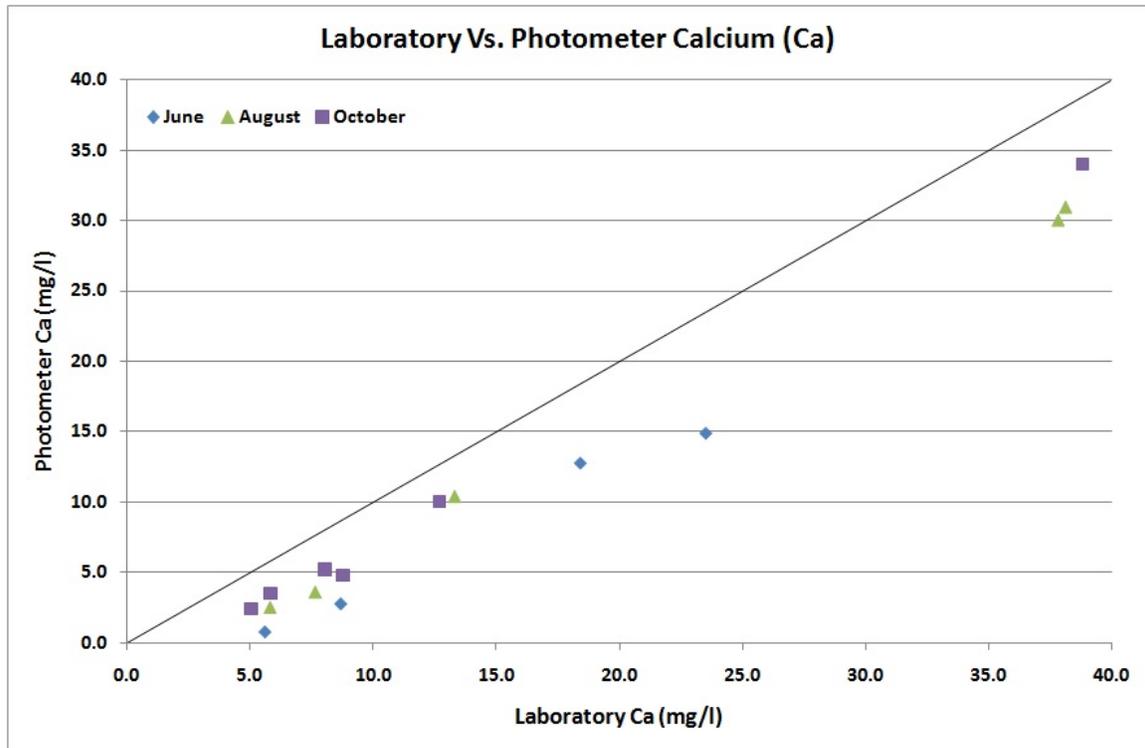


Figure 16. Calcium by photometer and laboratory.

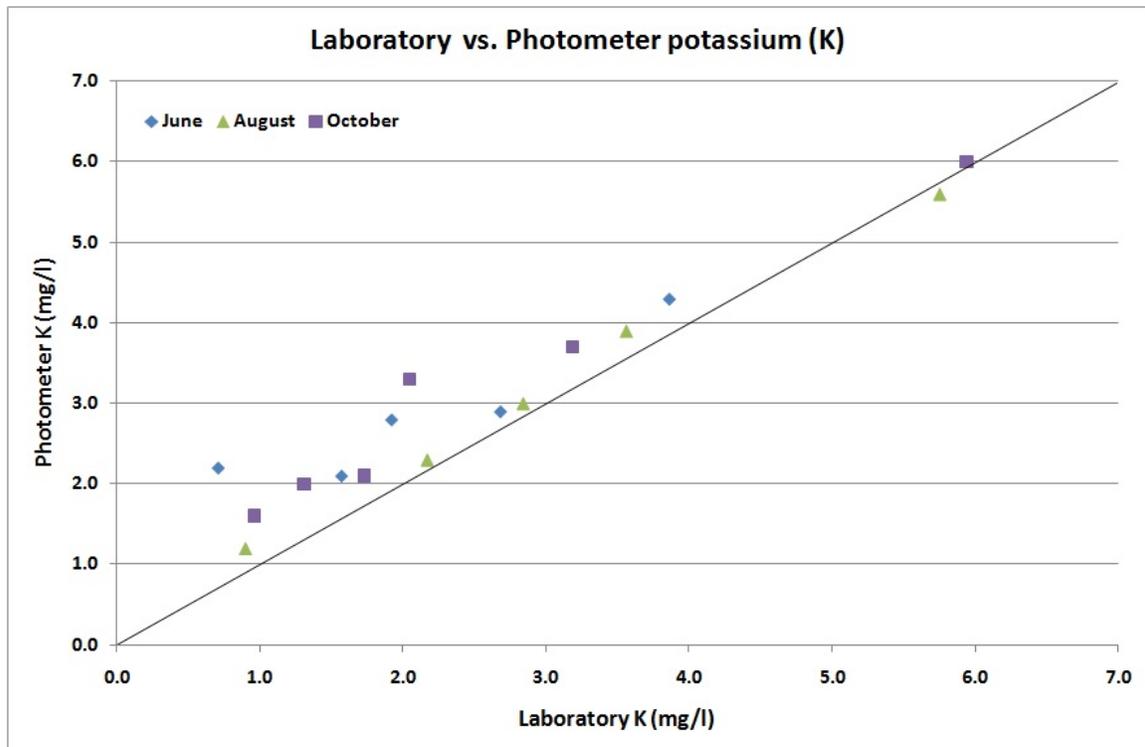


Figure 17. Potassium by photometer and laboratory.

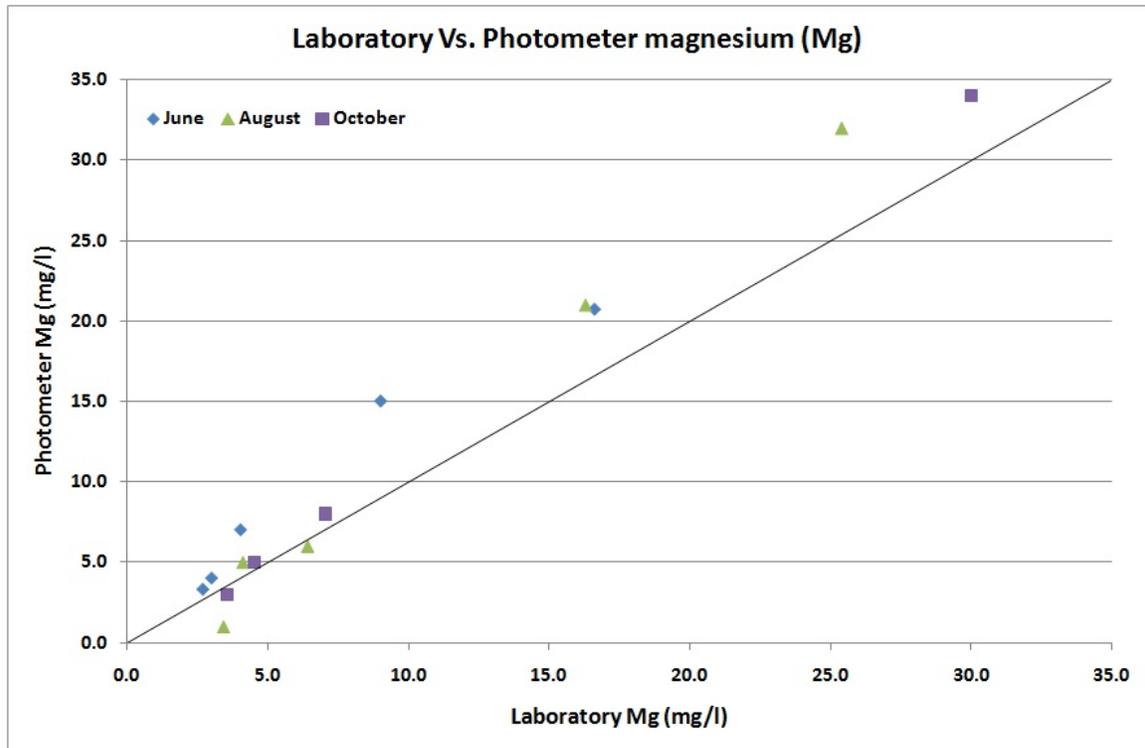


Figure 18. Magnesium by photometer and laboratory.

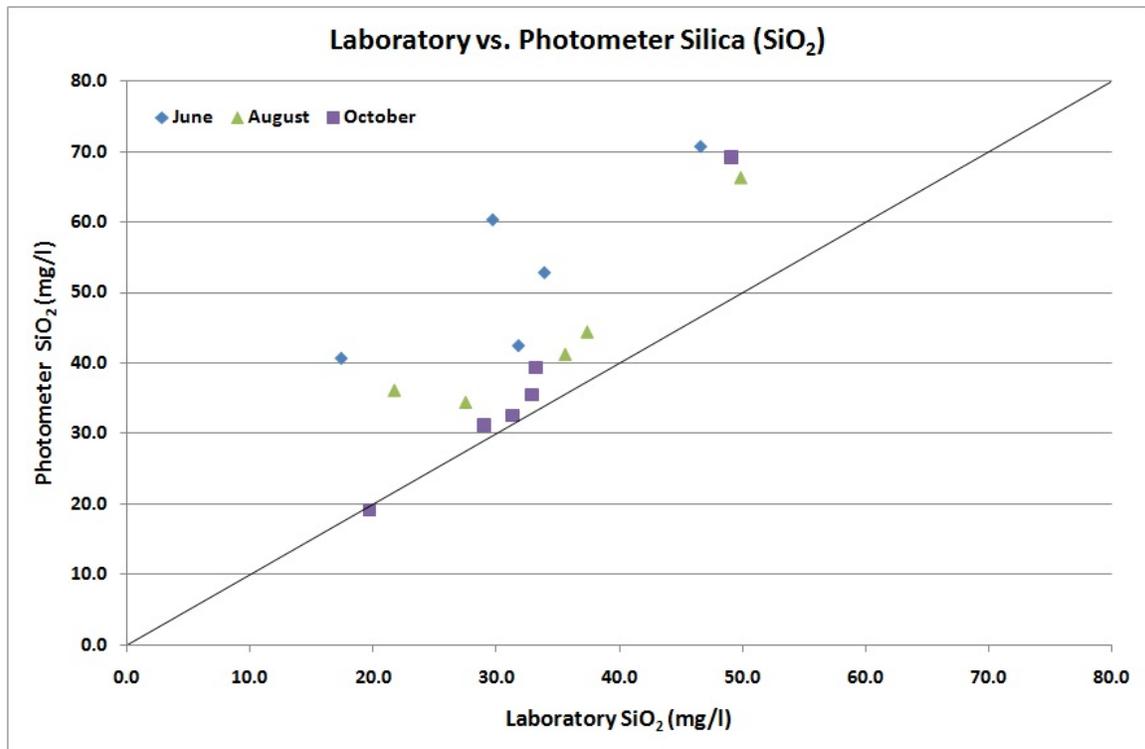


Figure 19. Silica by photometer and laboratory.

Extreme biases are illustrated by Al, Fe and Mn (Figure 20 to Figure 22). Preservation of the laboratory samples with HNO₃ did not improve the correlation with the photometer analyses although for Al, acidification of the sample did improve contrast since only about 15% of the non-preserved photometer results are above detection limits. The Fe has higher concentrations in the laboratory results, but the correlation between laboratory and photometer is weaker.

Calcicol displays good correlation, and no extreme bias like those mentioned above (Figure 16).

Fluoride (Figure 24) has a very strong photometer high bias, especially for June and August results. Most results appear to vary between 1.00 to 1.30 mg/l for the photometer and up to 0.20 mg/l for the laboratory. The reason for this discrepancy is unknown and warrants further investigation.

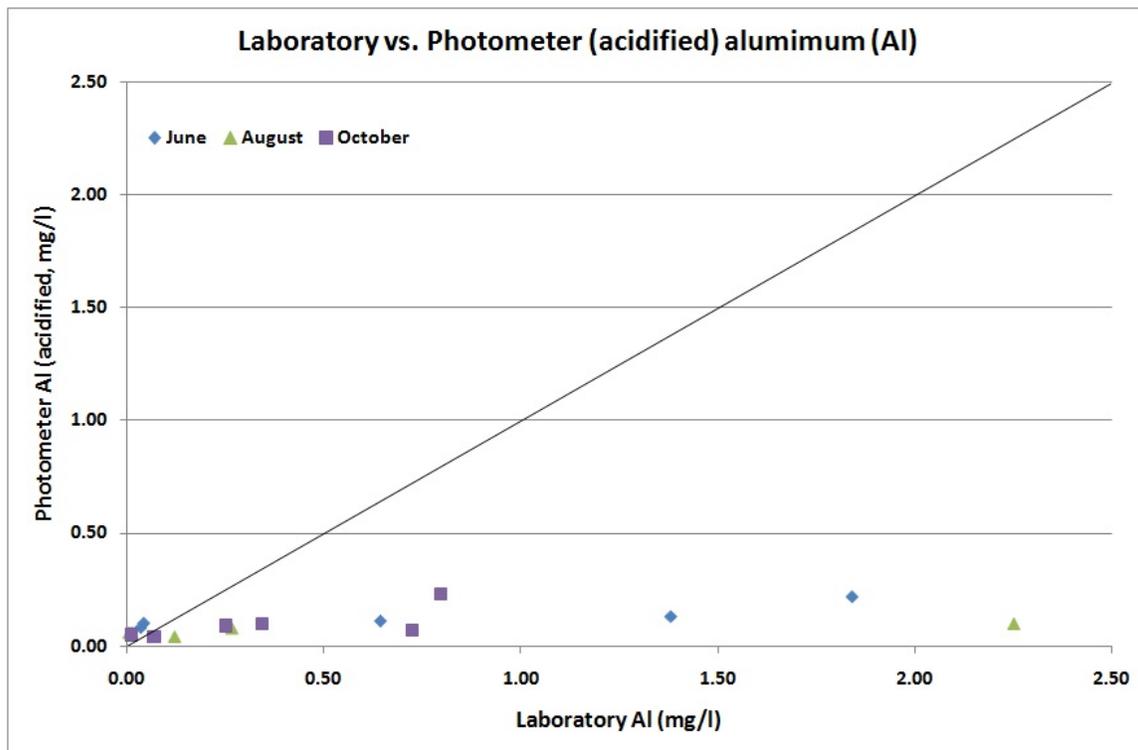


Figure 20. Aluminum (acidified) by photometer and laboratory.

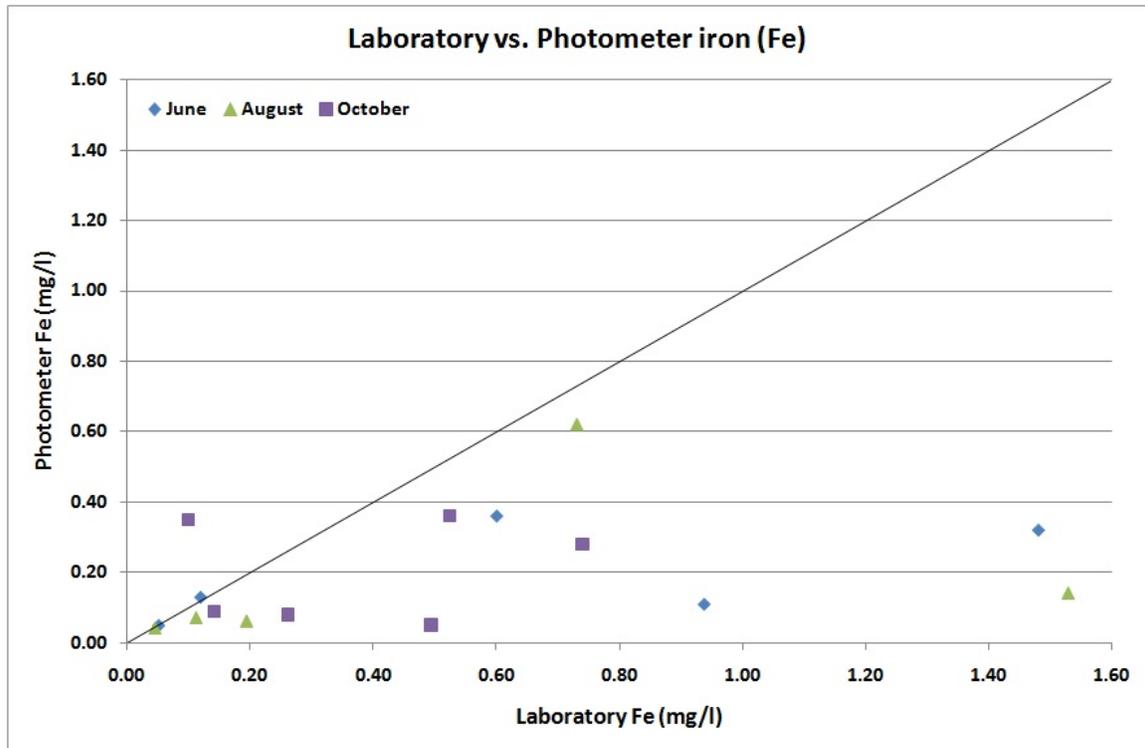


Figure 21. Iron by photometer and laboratory.

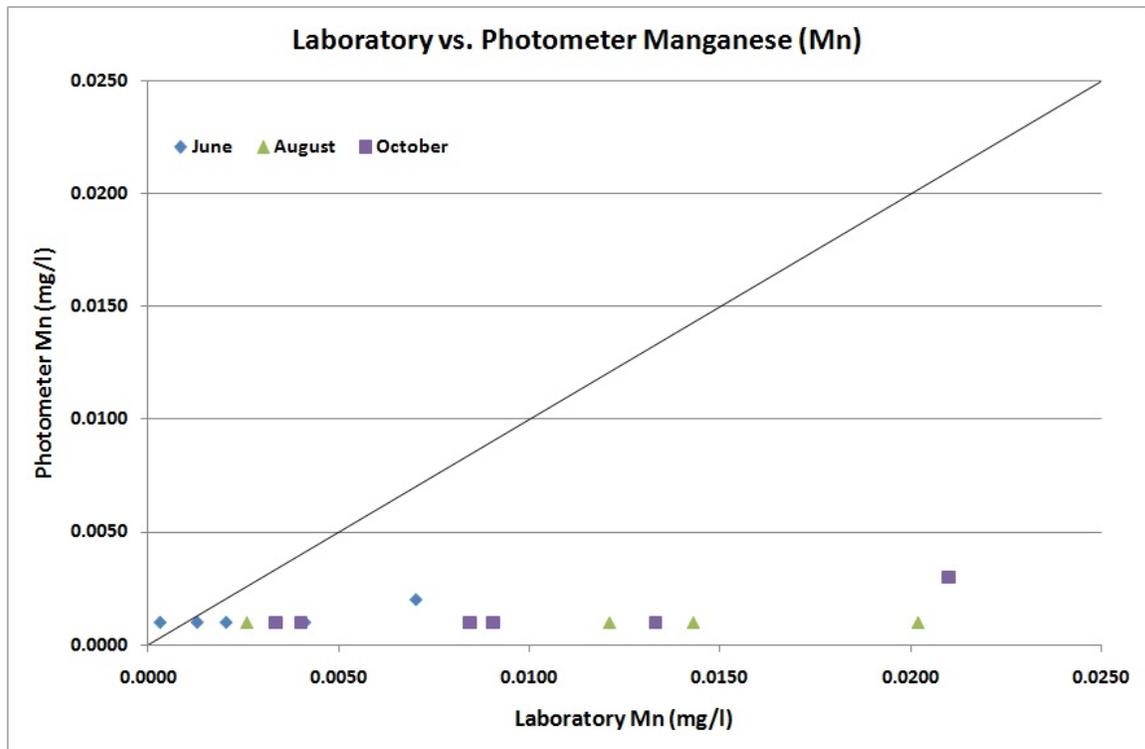


Figure 22. Manganese by photometer and laboratory.

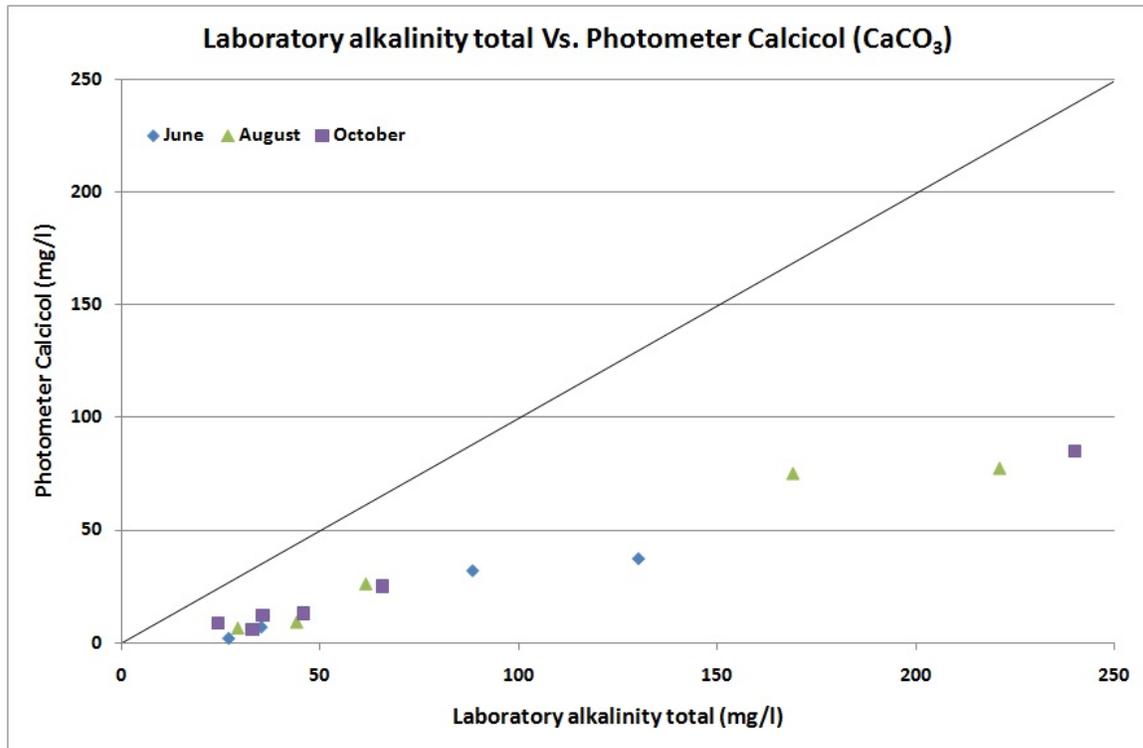


Figure 23. Calcicol by photometer and laboratory.

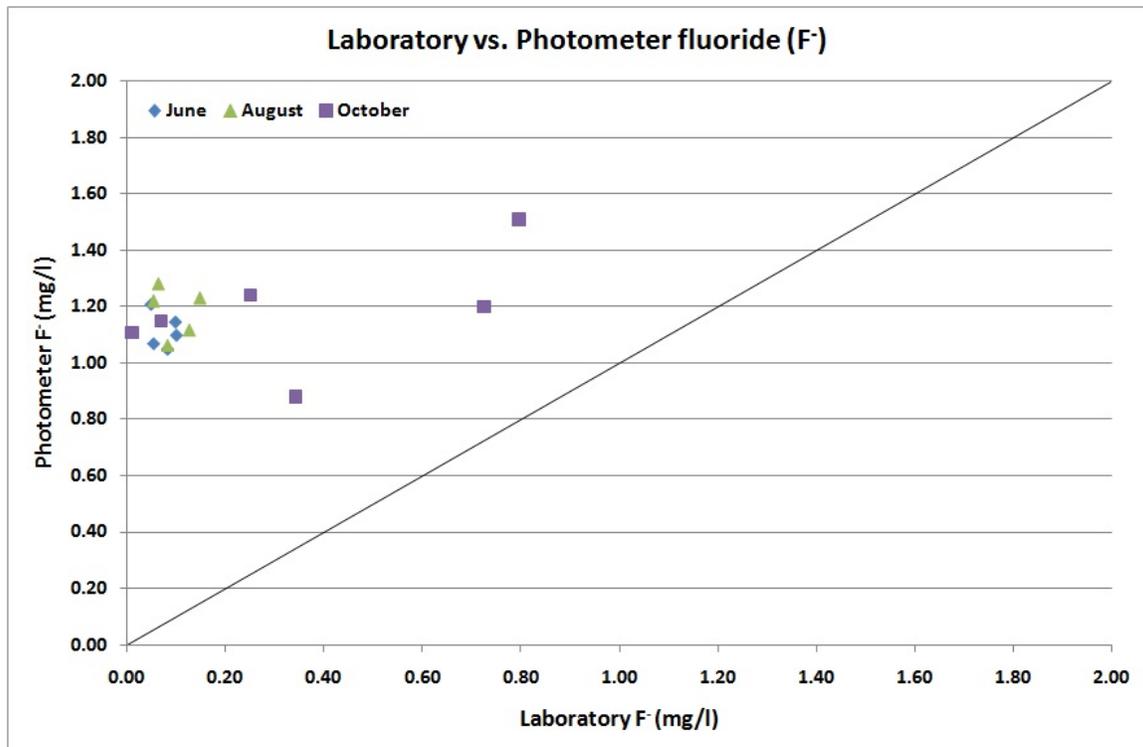


Figure 24. Fluoride by photometer and laboratory.

Turbidity, TDS, Conductivity and pH results

Turbidity results (Figure 25) show a high bias for the photometer, suggesting that the laboratory method is less sensitive. Laboratory turbidity tests have a 72 hours holding time requirement after shipping for stabilization, which might contribute to the observed difference, but the high bias, and the high level of colloids in some of the samples (Figure 50) are an indication that the holding time is probably not the main cause.

Conductivity, TDS and pH (Figure 26 to Figure 28) all show good correlations between field and laboratory determinations, although TDS has some scatter and a small high laboratory bias. This is due to the laboratory gravimetric test, which takes into consideration all the solids in the sample, including organics that the PCS Testr does not measure. A second TDS reading was done two months later on samples stored at the laboratory; the same differences were observed.

The pH results show a slight scatter, but correlate well with laboratory measurements.

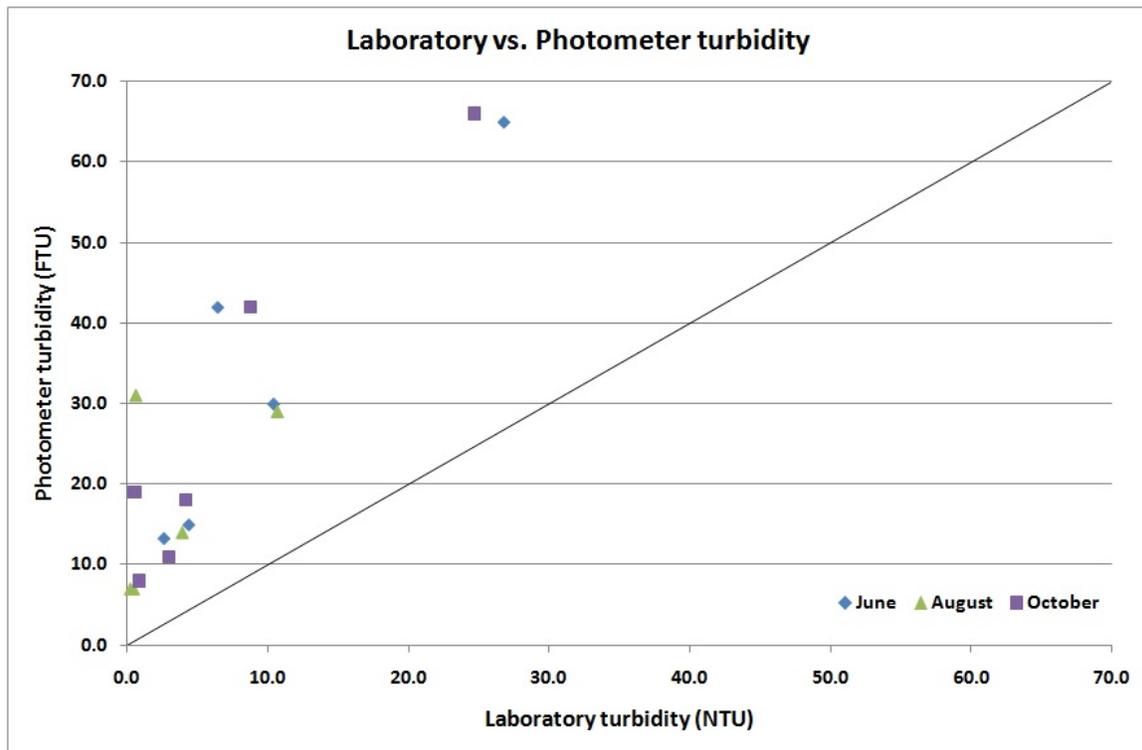


Figure 25. Turbidity by photometer and laboratory.

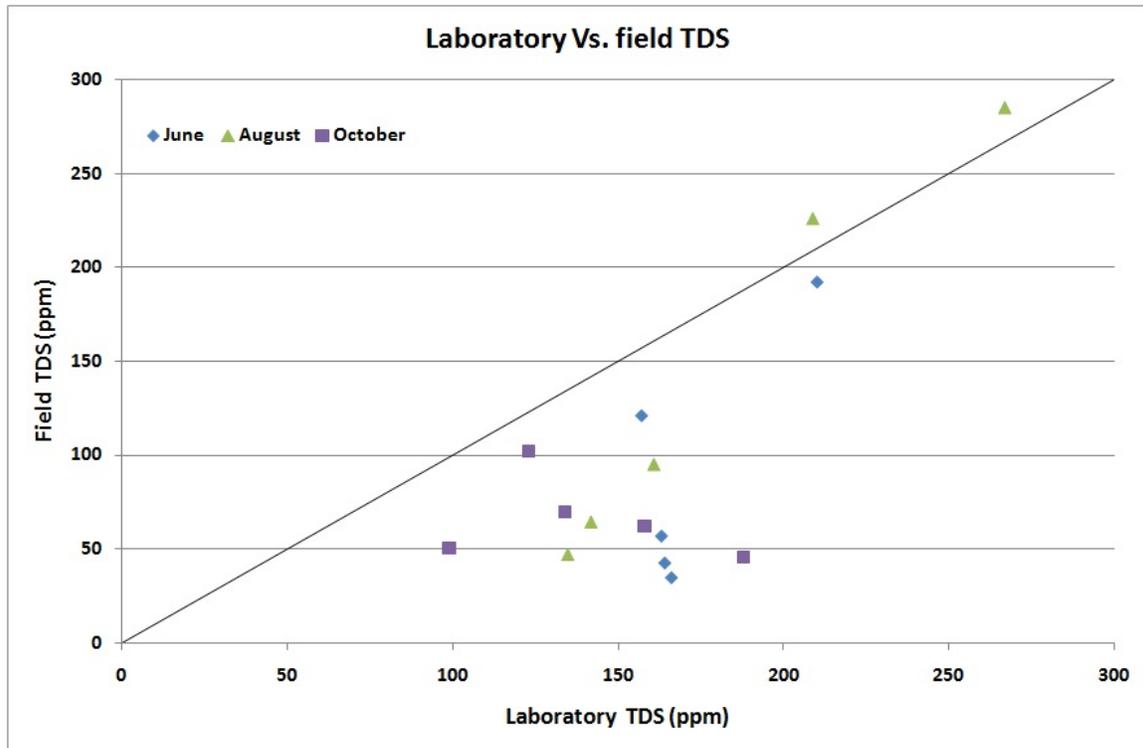


Figure 26. TDS by photometer and laboratory.

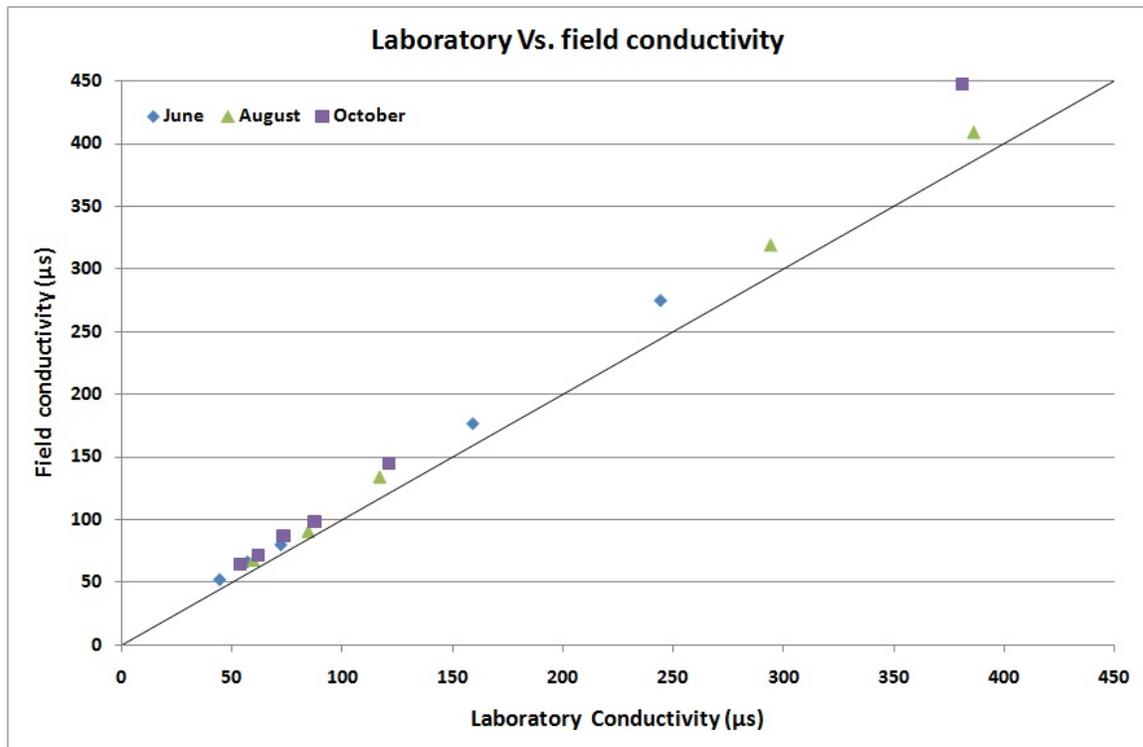


Figure 27. Conductivity by Oakton PCS Testr 35 meter and laboratory.

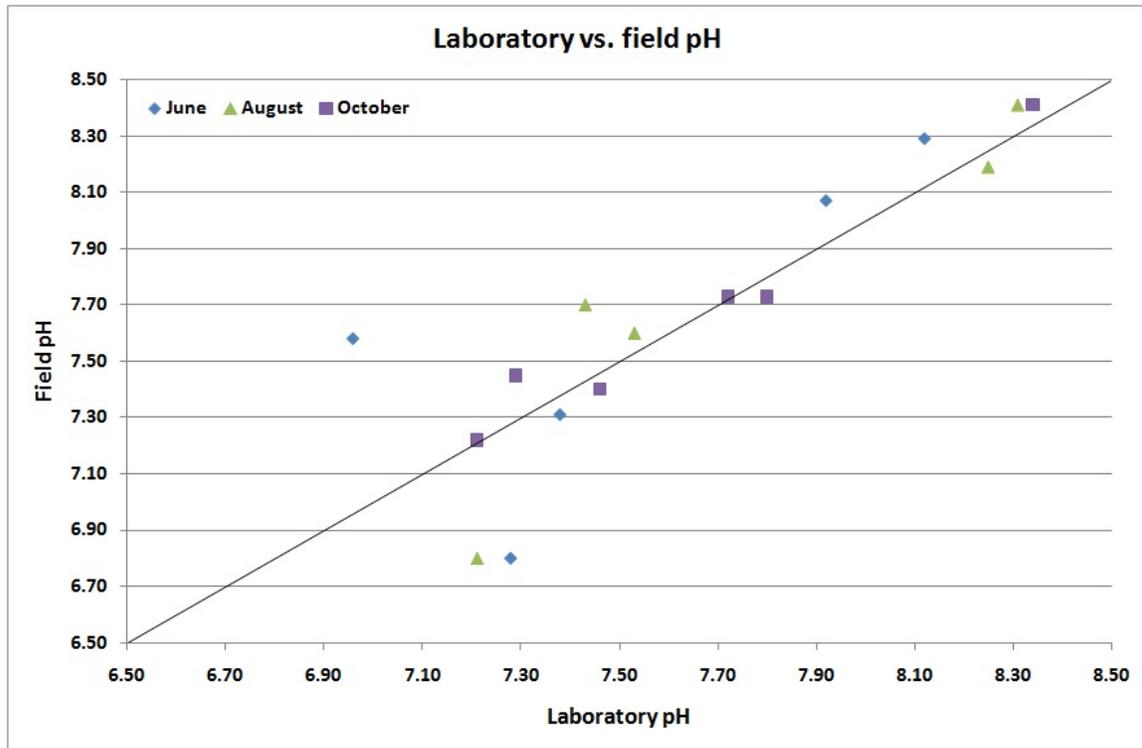


Figure 28. pH by Oakton PCS Testr 35 meter and laboratory.

Seasonal and Daily Variation

One of the objectives of this study was to investigate seasonal and daily variations. The area is hydrologically complex due to the variety of standing water bodies present. These include lakes of different sizes (natural and beaver dammed) occurring at a range of elevations, complex water courses running into and out of these lakes as well as hard to identify ground water discharge sites. Investigation was done by monitoring the changes in the water chemistry through the analysis of repeated water samples collected at a base station shown in Figure 4 (sample point #011 just west of Bob MINFILE location) in June, August and October. Throughout the survey, the heavy and scattered precipitation raised the concern about the possibility of large fluctuations in analyte concentrations. To better understand the daily (diel) cycles, daily monitoring was initiated at the same base station in June.

Seasonal Variation

Analyte concentrations in water could be affected by various factors including dilution and input of solids during periods of accelerated weathering. For this study area, the assumption is that there should be more dilution in spring and early summer due to greater precipitation and runoff from snowmelt, as well as an increased discharge of groundwater into the drainages. High groundwater discharge is also expected in summer although groundwater levels are expected to decrease resulting in diminished dilution from both rainfall and groundwater in the fall. pH values should be at their lowest (more acidic) during the fall when groundwater discharge is lowest, and analyte concentrations are higher. In turn,

the lower pH allows for greater dispersion of cations in solution. In alkaline waters the pH would be buffered.

Central BC was wetter than average in 2016 (Figure 29) and, while the average precipitation for April was similar to May, the overall spring rainfall for this period was greater than in 2015. Rainfall increased in July and August and seasonal precipitation trends for the area followed previous annual local climate cycles. Ideally, higher precipitation would dilute element concentrations in surface water and elevate the water table.

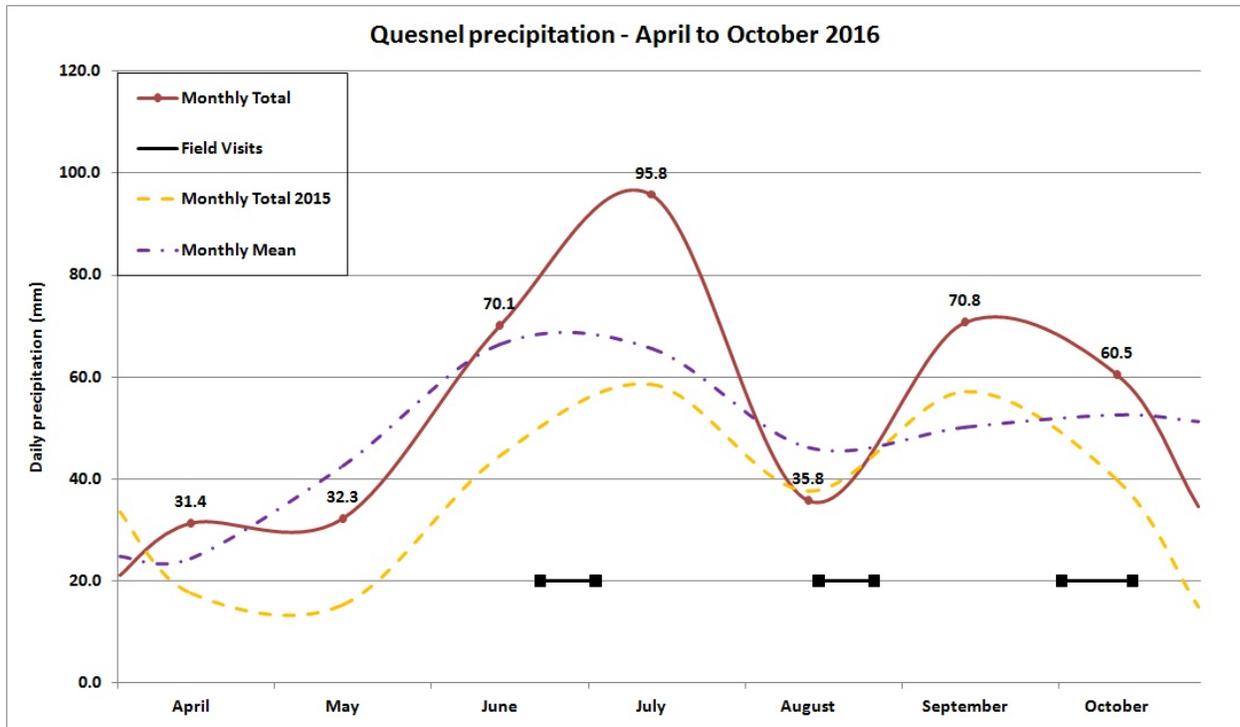


Figure 29. Simplified Quesnel precipitation chart. Refer to Figure 3 for daily variations.

Daily Variation

Field conditions were monitored at the base station where various daily measurements were collected (Figure 30). Base station monitoring helps with our understanding of how analyte concentrations vary over short intervals and enables us to estimate the effect of precipitation on erosion and input of solutes into streams.

Data was collected every day during the early to mid-afternoon. Conductivity, TDS, salinity and pH were measured using the PCS Testr 35 meter, and a small water sample was collected for photometer SiO_2 analysis due to its seasonal stability (Yehia and Heberlein, 2015).

While the information collected sheds light on variations in daily field conditions, the precipitation data is not local to the study area. In hindsight, rainfall could have been measured with a rain gauge at the base station, but since the idea of installing a base station was only thought of during the first field visit,

data from the nearest Environment Canada station at Quesnel had to be used throughout for consistency. Due to the distance and elevation differences between Quesnel and Nazko, some of the rainfall data does not reflect the local precipitation history. For example, on the night of October 5th, there were heavy showers in the study area, but no rain was recorded in Quesnel until October 7th. Stream water chemistry responds to local rainfall with conductivity, TDS and salinity all decreasing, and pH rising due to the increased dilution.

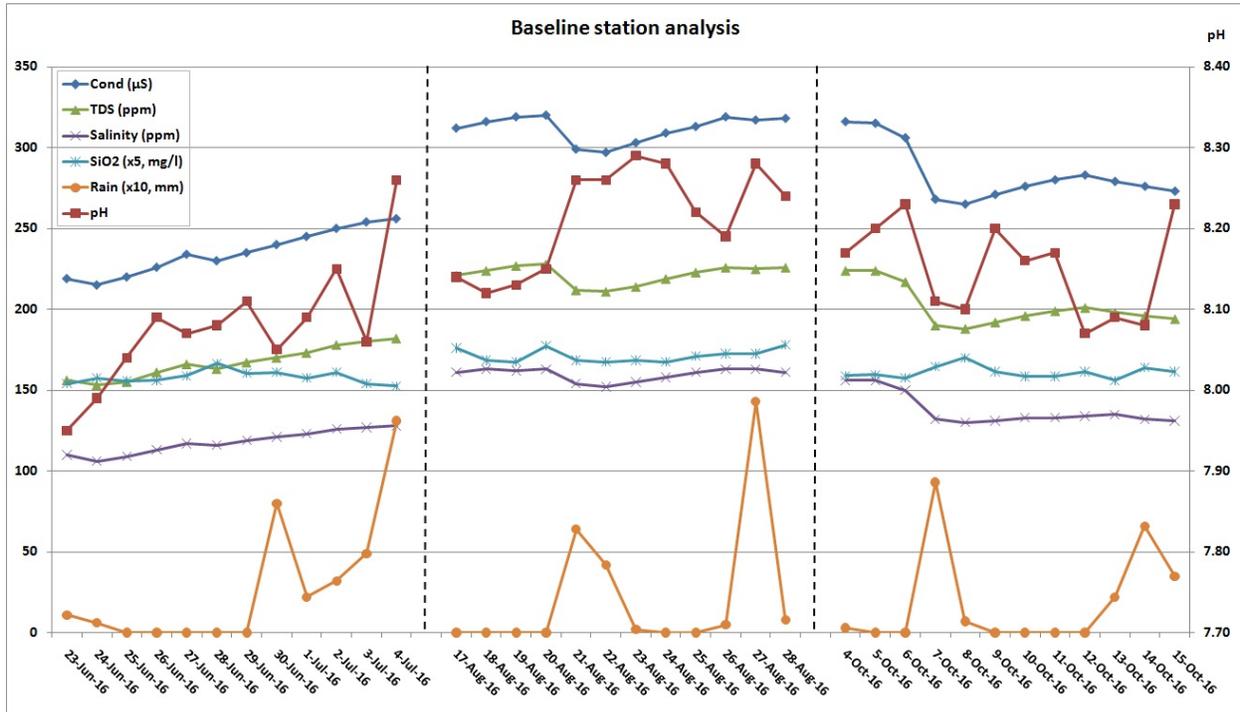


Figure 30. GPS #011 Hydrogeochemistry base station. Note that rain and SiO₂ are enhanced for visual comparison.

Analyte concentrations increased steadily through June, but were lower than August and October. Figure 30 also shows that there were pH fluctuations. These could be the result of local hydrology since the fluctuations are quite small, or of instrument noise in the order of the 0.02 pH unit range. The concomitant pH increase with greater dilution could reflect the possible alkaline nature of the creek's groundwater source.

August conditions were stable with some observed responses to the precipitation in the mid-to late parts of the month. After the first rainfall, concentrations for most parameters dip slightly and then gradually recover to pre-rain levels. pH shows an abrupt increase after the first rain event, which is interpreted to reflect an influx of more alkaline ground water into the drainage. There is insufficient information to reveal similar patterns after the second rain event late in the month.

October and August patterns are very similar. After the first rainfall on October 7th, conductivity, salinity and TDS all display a notable drop while SiO₂ concentration shows a slight increase. Salinity values remain depressed for the remainder of the sampling period while TDS and conductivity recover somewhat but do not reach pre-precipitation levels. Stream water pH shows a decreasing trend in

response to the precipitation events although the second decrease in pH begins before the rainfall on October 14th. The pH decrease is probably a reaction to local precipitation, which is not recorded at the same time due to use of rainfall data from a remote weather station.

Figure 30 reveals some interesting insights into the effects of precipitation on creek water chemistry. June generally behaves as expected, but concentrations continue to rise and remain stable regardless of the increased precipitation. October concentrations are lower than August, while the opposite trend was expected and this could be a unique event for 2016. Similar to the variation previously reported by Yehia and Heberlein (2015), SiO₂ is extremely stable regardless of conditions, with concentrations varying between 30.8 to 35.6 mg/l throughout the entire survey.

Analyte Results

The effect of rainfall and other seasonal changes on analyte levels can be demonstrated by (1) plotting the seasonal measured concentrations at each site and by (2) plotting results for each season in order of increasing concentration. The first plot is useful since it compares concentrations directly by season at each site, while the second provides an overall seasonal comparison.

Charts for Cu (free and total), MoO₄, and SO₄ do not include data for June. This is because the August turbidity analysis (more below in the turbidity section) revealed false trends in the photometer results. Charts for Ni and Zn (EDTA) are not included because there is insufficient data for interpretation.

Commodity Elements

Data is available for some commodity elements including Cu, Fe, MoO₄ and Zn+Cu (Figure 31 to Figure 35). Except for Fe, all elements display a strong seasonal variability. As expected, concentrations for Cu (free and total, Figure 31 and Figure 32) and MoO₄ (Figure 33) were highest during the October survey. This may be the result of higher concentrations caused by decreased groundwater discharge (i.e. less dilution of the surface water). The two most anomalous samples, Stations 013 and 041, lie downstream from large bogs. The values for these two points are highest in August and not October suggesting that Fe is released from reduced, organic soil into the stream water, while lower values in October are caused by higher dilution levels resulting from precipitation in September.

Iron shows very little seasonal variation (Figure 34), except for its highest values in the August results. In comparison Zn+Cu (Figure 35) displays strong seasonal differences.

Of note are stations 012 and 035. At station 012, there is a strong correlation between dissolved and total Cu concentrations in the photometer and PDV results. They also match the MoO₄ and SO₄ (Figure 33 and Figure 46) results, and are two of the highest values for Zn+Cu in June. Station 012, situated to the southwest of the Bob occurrence likely reflects the presence of mineralization higher up in the catchment basin. Station 035 has elevated MoO₄ and has a good correlation with Zn+Cu. This relationship could be caused by the higher turbidity values recorded at that location.

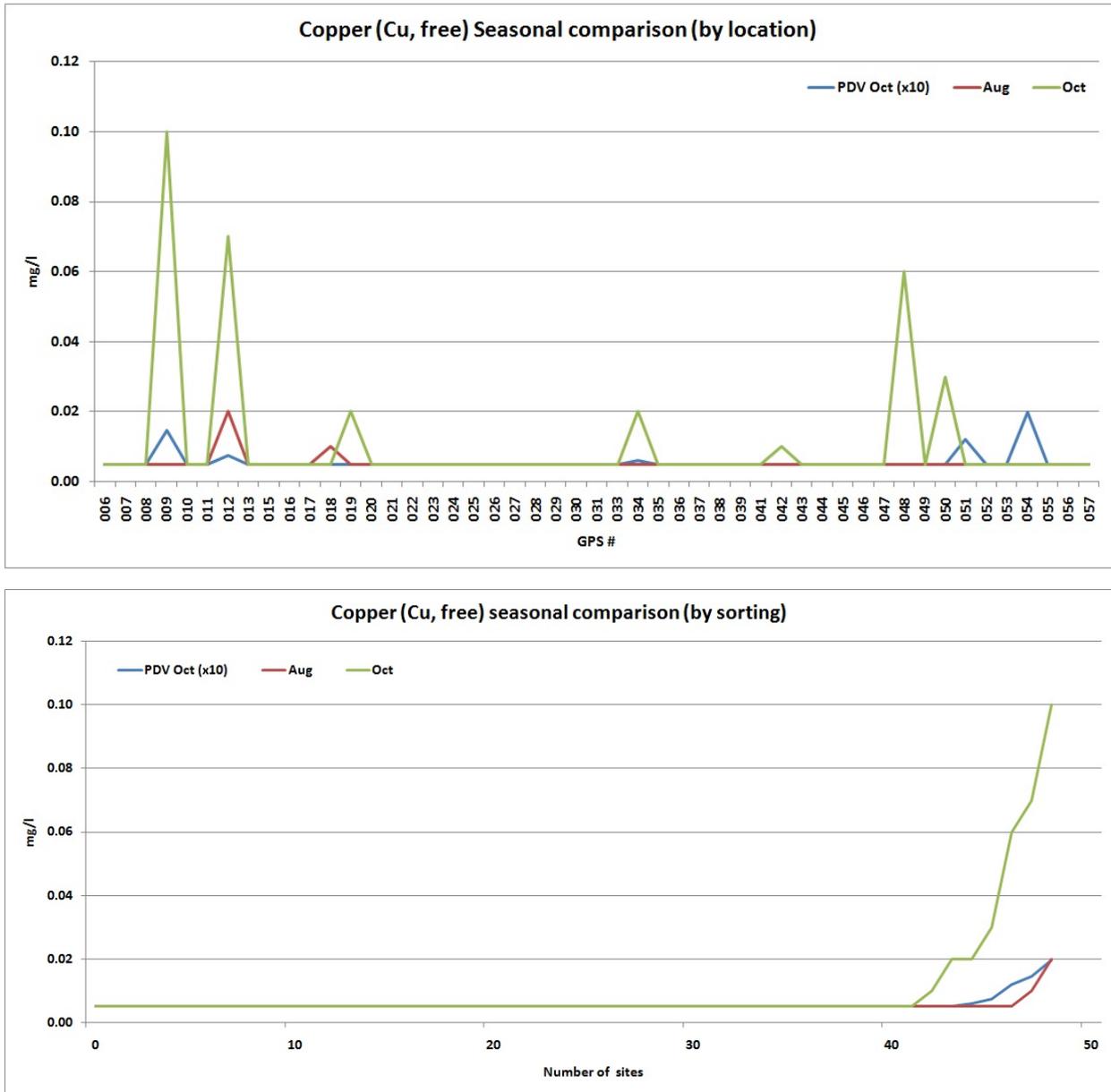


Figure 31. Copper (free) seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

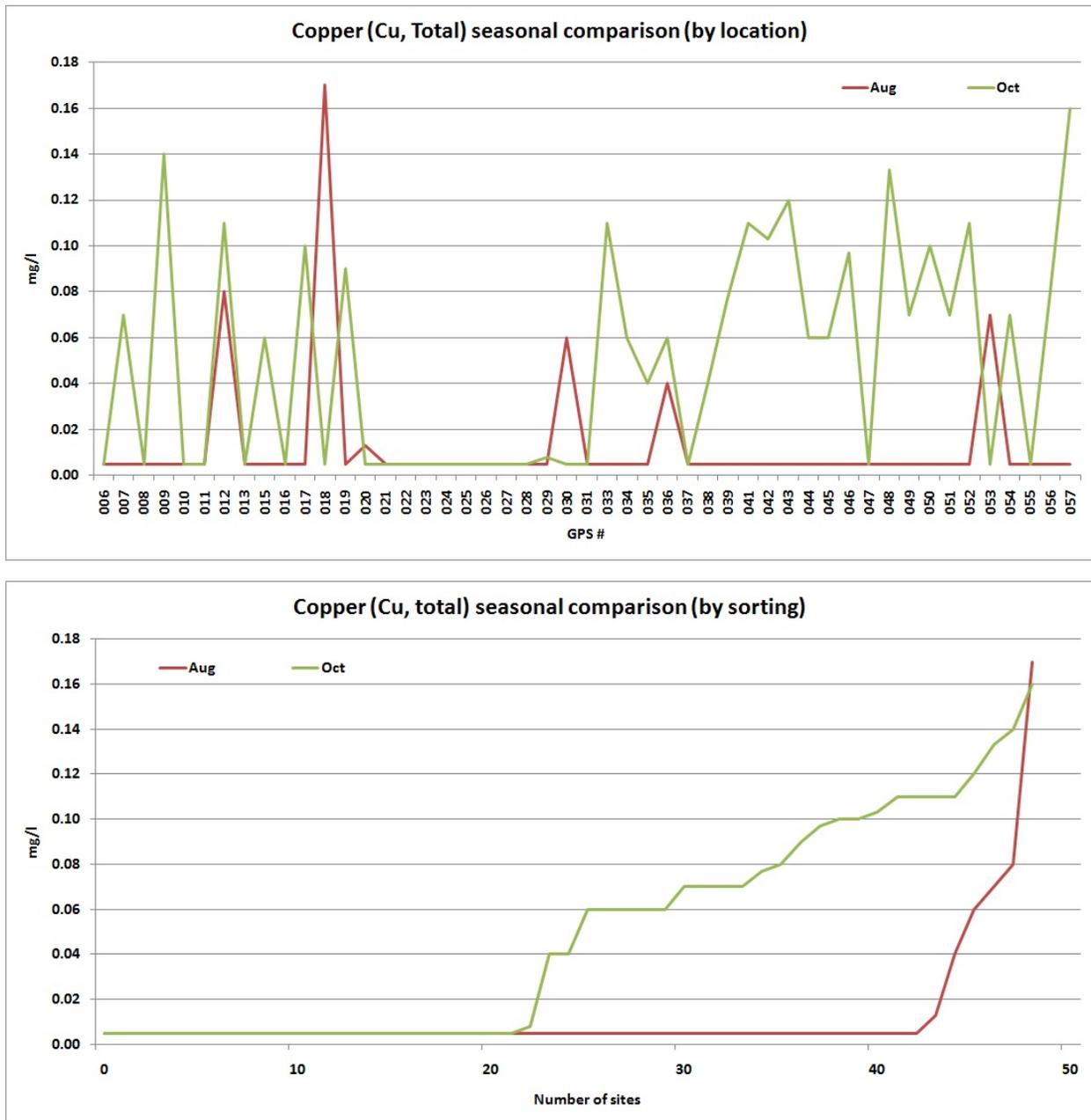


Figure 32. Copper (total) seasonal comparison by location (top) and seasonal comparison by sorting in order of increasing concentration (bottom).

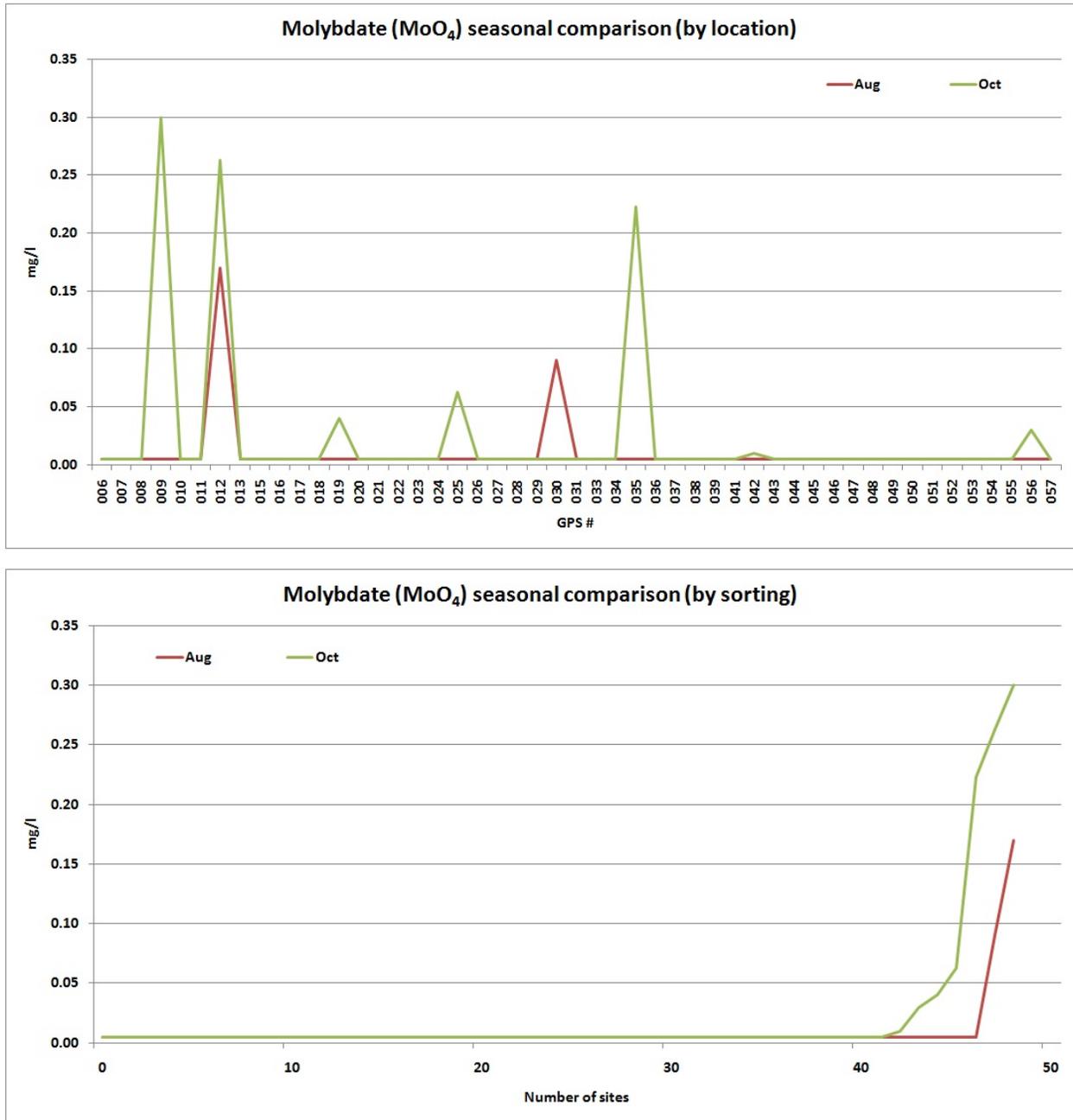


Figure 33. Molybdate seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

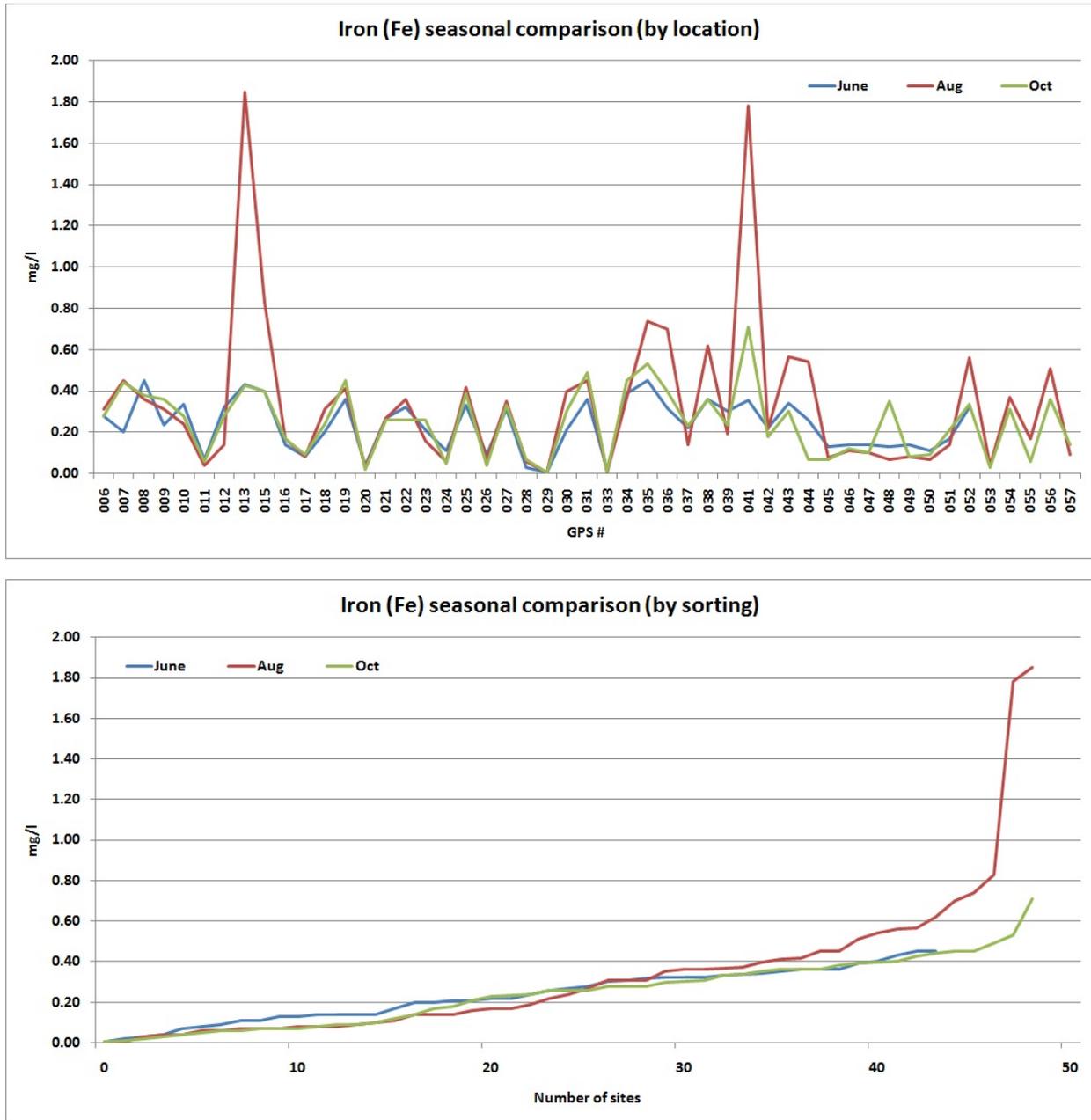


Figure 34. Iron seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

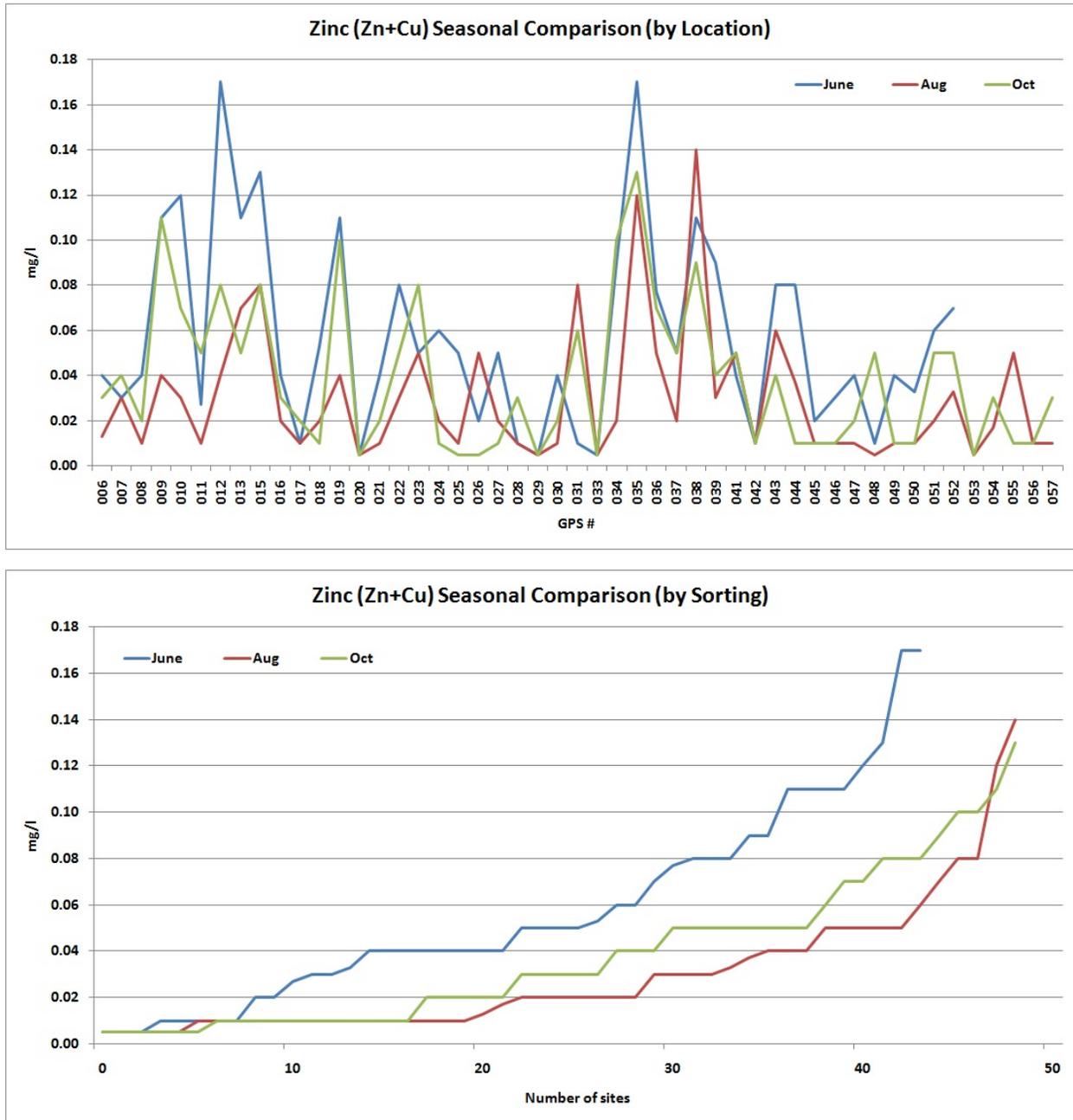


Figure 35. Zinc (Zn+Cu) seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

Other Elements and Anions

Figure 36 to Figure 46 show other photometer test results that indicate the effect of seasonal variations on water chemistry.

Aluminum (acidified, Figure 36) displays the strongest response to weathering of all the analytes. This is evident from the Al measured at individual sample stations that varies considerably between seasons and sometimes has even a strong negative response in the August results (for example station 009 in the range of 0.18 mg/l). Sorting shows a wide gap in seasonal concentrations, with concentrations becoming elevated during times of increased precipitation.

Even though there are only three As results (Figure 37) above detection limit (stations 7, 17 and 54), the correlation of As from month to month is remarkably consistent. August concentrations are slightly higher; again, possibly due to increased precipitation in October. It appears that the October precipitation did not affect As concentrations as significantly as it did for some other analytes. No PDV data was collected in June for these locations.

Calcicol (alkalinity) and Hardicol (hardness) results are shown in Figure 38 and Figure 39. Both show consistent results between seasons. Alkalinity displays a gradual increase with the lowest concentrations in June and the highest in October.

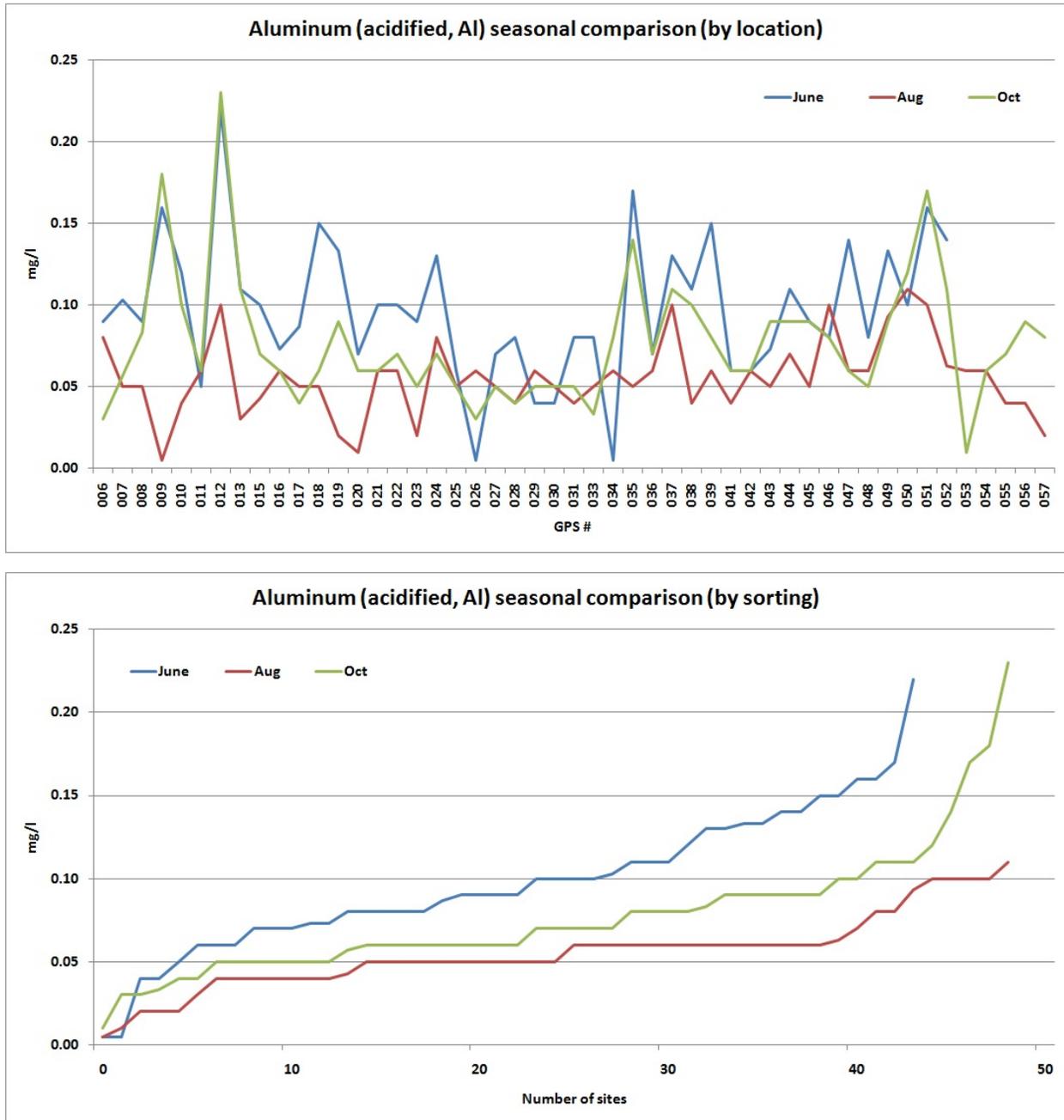


Figure 36. Aluminum seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

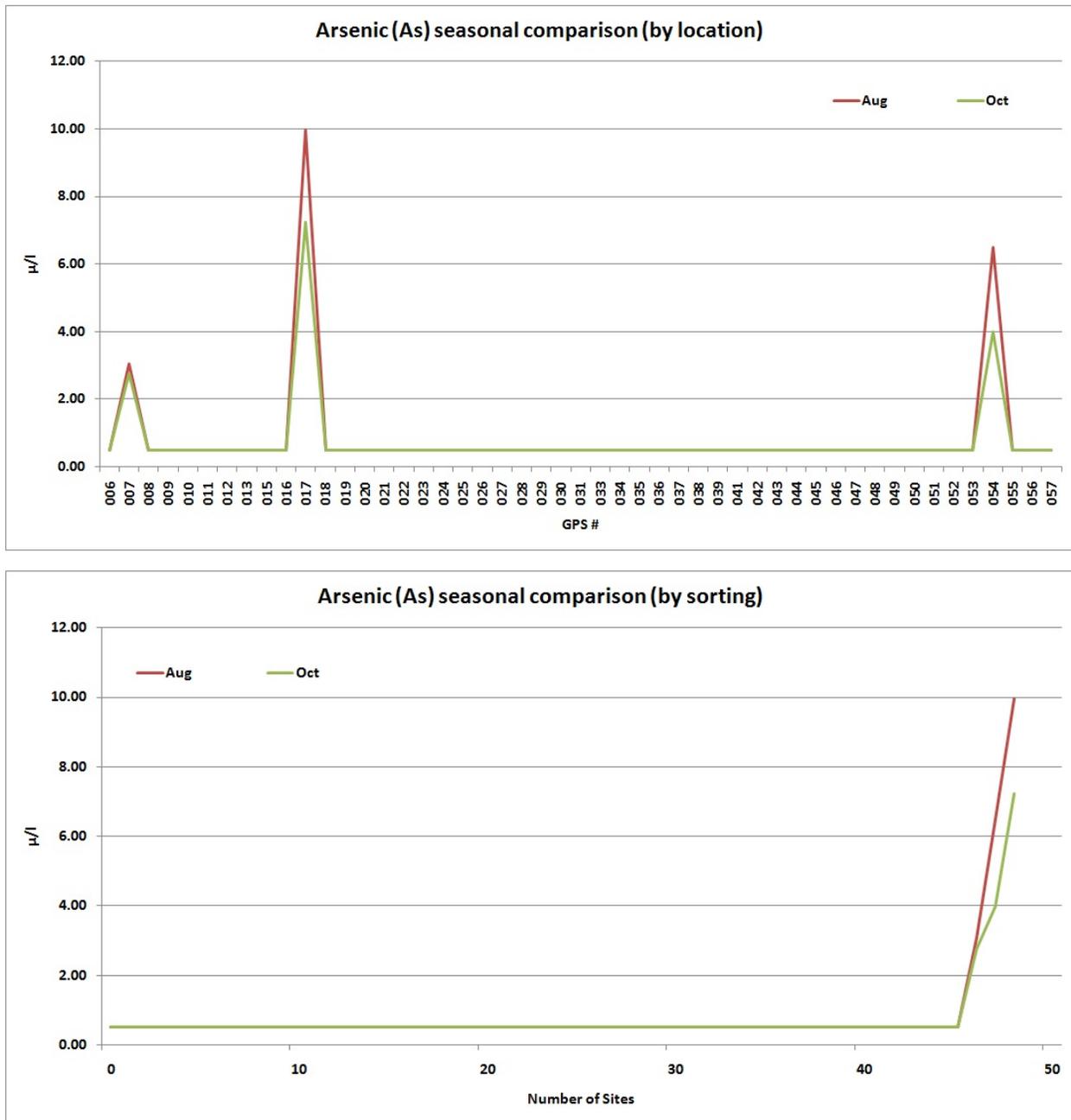


Figure 37. Arsenic seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom). Note units are in micrograms per litre in this figure only.

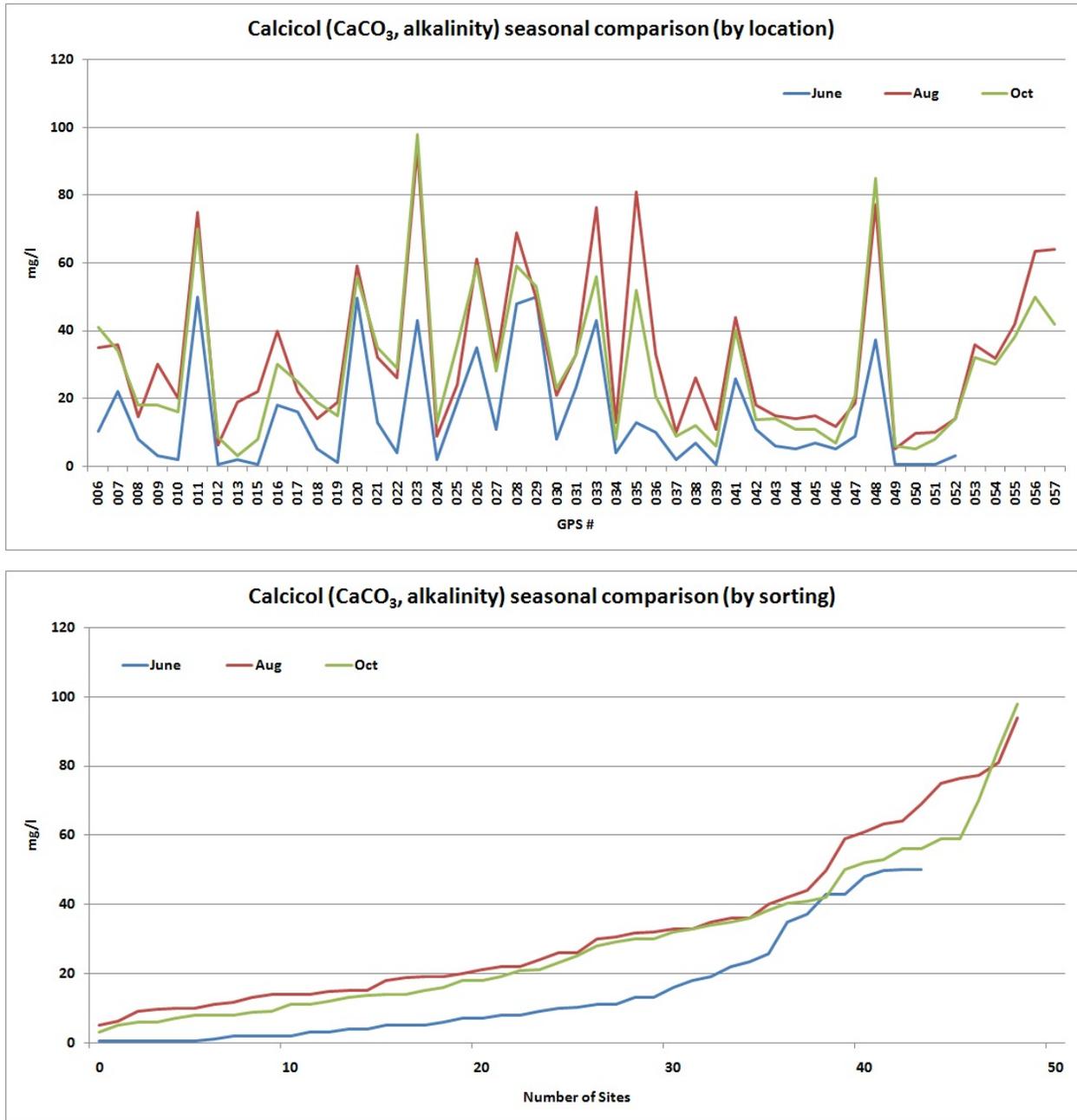


Figure 38. Calcicol seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

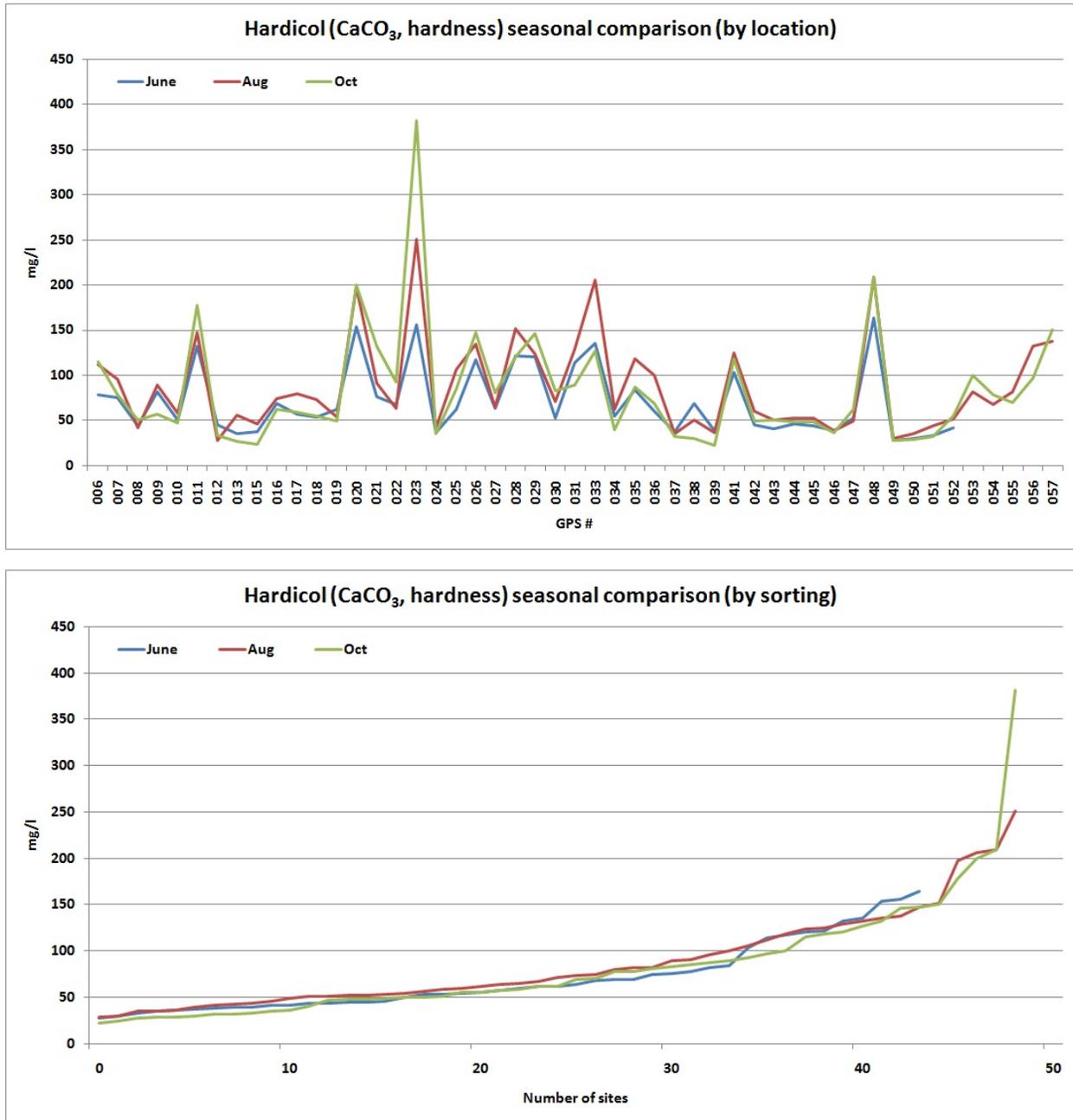


Figure 39. Hardicol seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

Chloride (Figure 40) concentrations vary between detection limit and 7.0 mg/l. The reason for the variation is unknown but may be partly attributed to the turbidity effect on the photometer tests at low concentrations. Individual sample stations do not show consistent Cl^- concentrations across the sampling campaigns. June especially has a quite high concentration compared to August and October.

Fluoride results (Figure 41) are different from the other analytes. Seasonal variability is quite marked at each sample location with some even displaying negative peaks, all within a narrow concentration range of 0.60 to 1.50 mg/l. The sorted results also show a markedly different trend by displaying a logarithmic curve instead of exponential. The results don't seem to show any consistent patterns, and may appear to represent just noise.

Potassium (Figure 42) is also relatively consistent between seasons. The reason for the three high peaks in June is unknown.

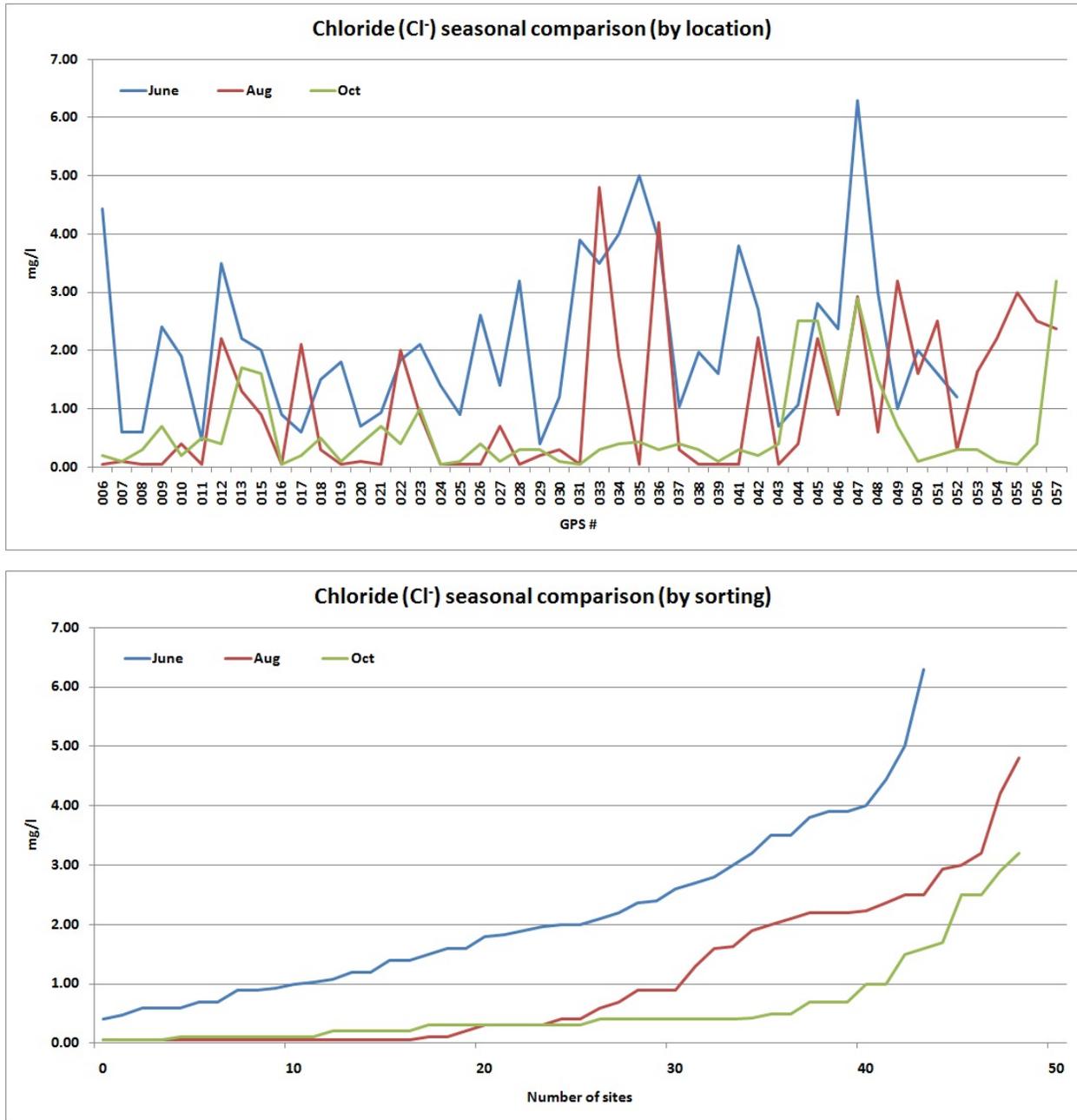


Figure 40. Chloride seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

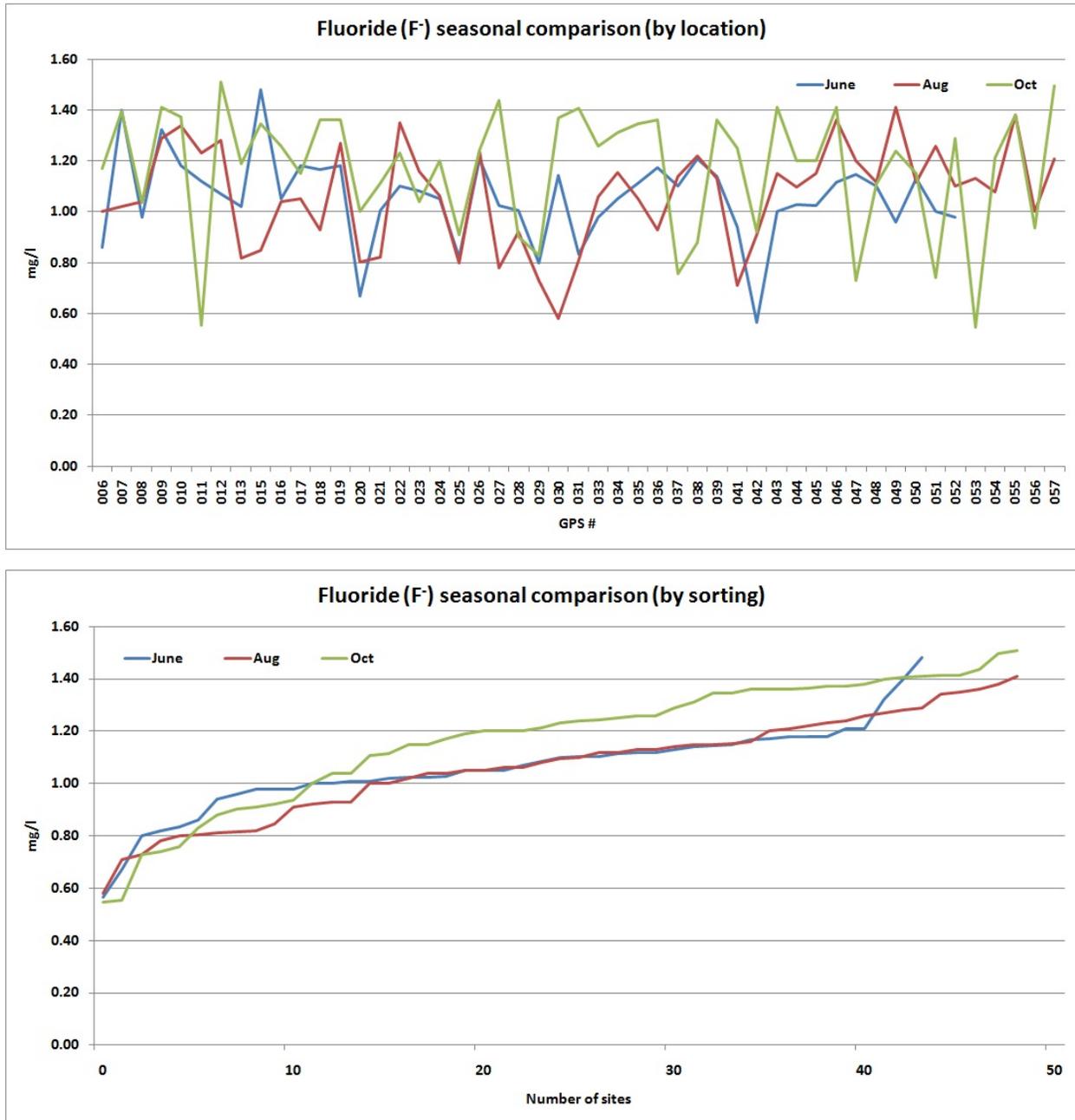


Figure 41. Fluoride seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

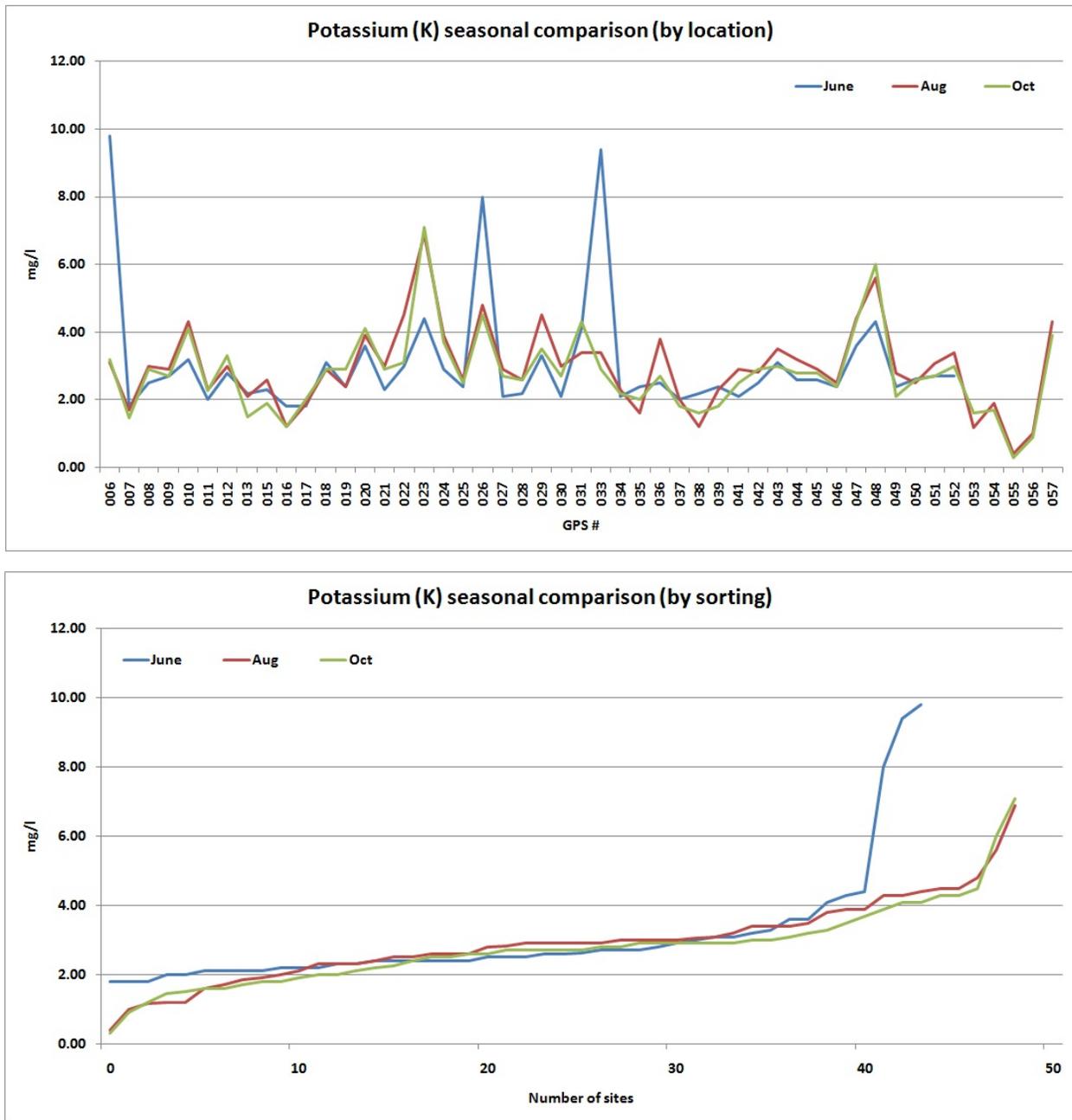


Figure 42. Potassium seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

Magnesium (Figure 43) shows excellent reproducibility between seasons. Part of the Mg stability may be the reagent procedure that calls for one tenth dilution with deionized water. This minimizes turbidity interference. Of the two highest peaks station 023 is about 2 km downstream from station 048.

Due to the low Mn (Figure 44) concentrations and narrow range, 0.001 to 0.007 mg/l, we do not have a clear picture of its seasonal behaviour.

Silica (Figure 45), like Al, is another analyte showing clear seasonal differences. Most values fall within a narrow range of about 25 to 60 mg/l. Sorting shows the expected seasonal behaviour, with decreasing concentrations over time. The patterns are similar between seasons but the concentrations are different.

Finally, SO_4 (Figure 46), an important mineralization indicator, displays low concentrations (1.0 to 14.0 mg/l). The reagent's sensitivity to turbidity at these levels makes the results vary significantly between sampling campaigns. Note, that at station 012 near to the Bob prospect, SO_4 is strongly correlated with Cu and MoO_4 .

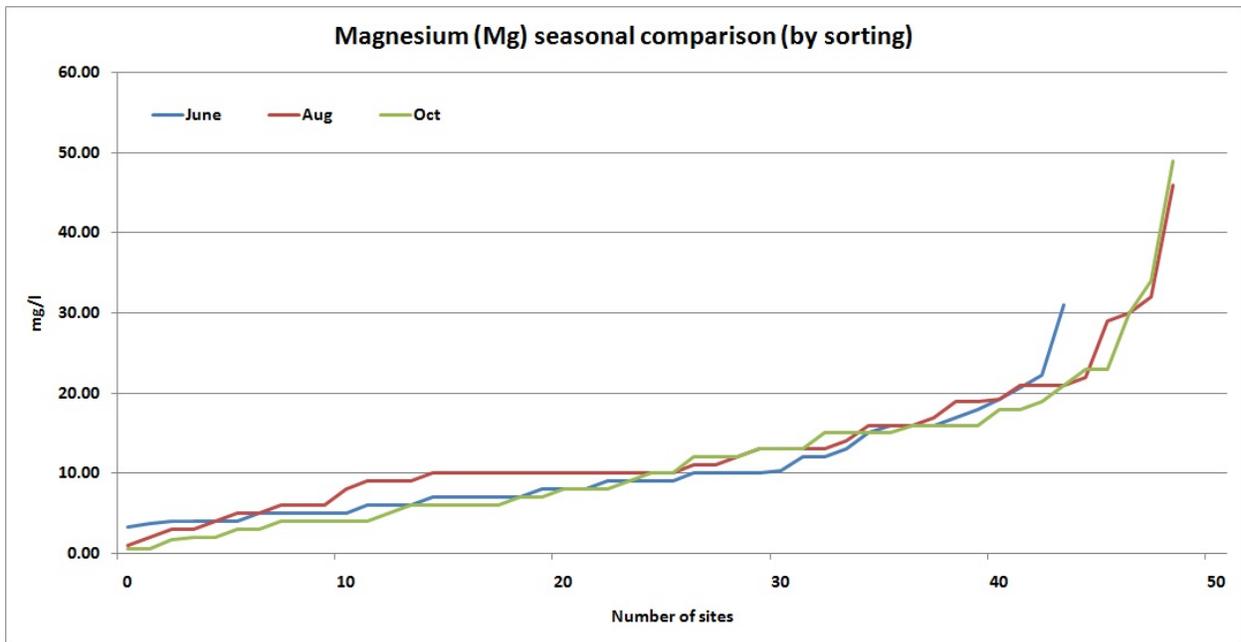
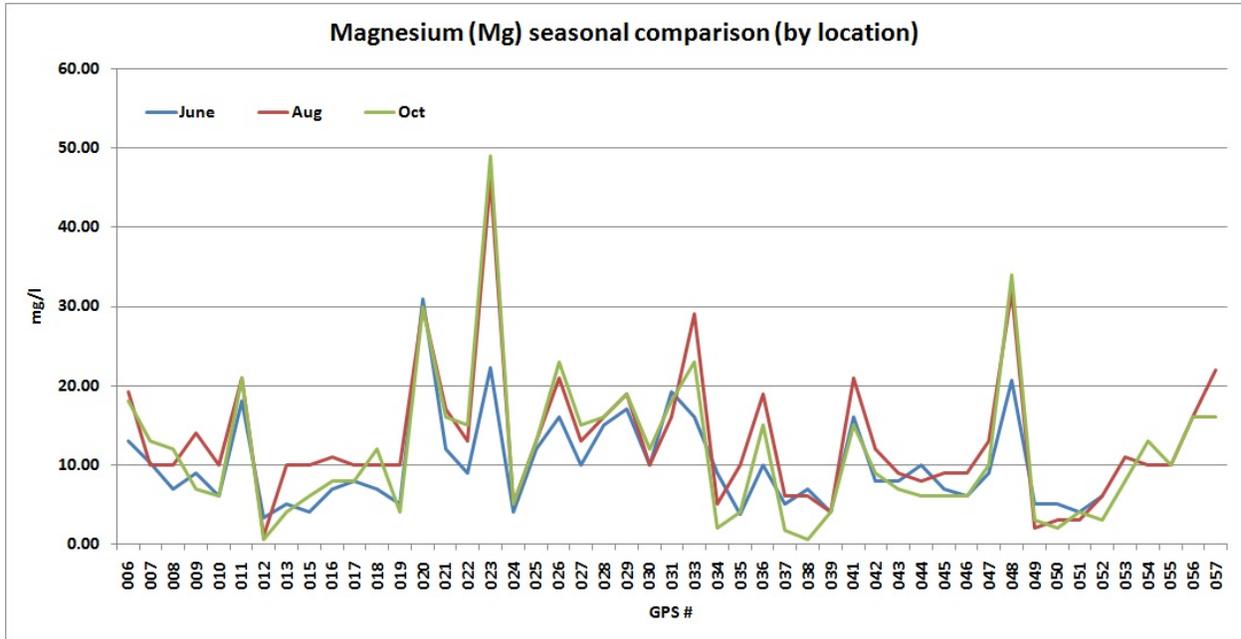


Figure 43. Magnesium seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

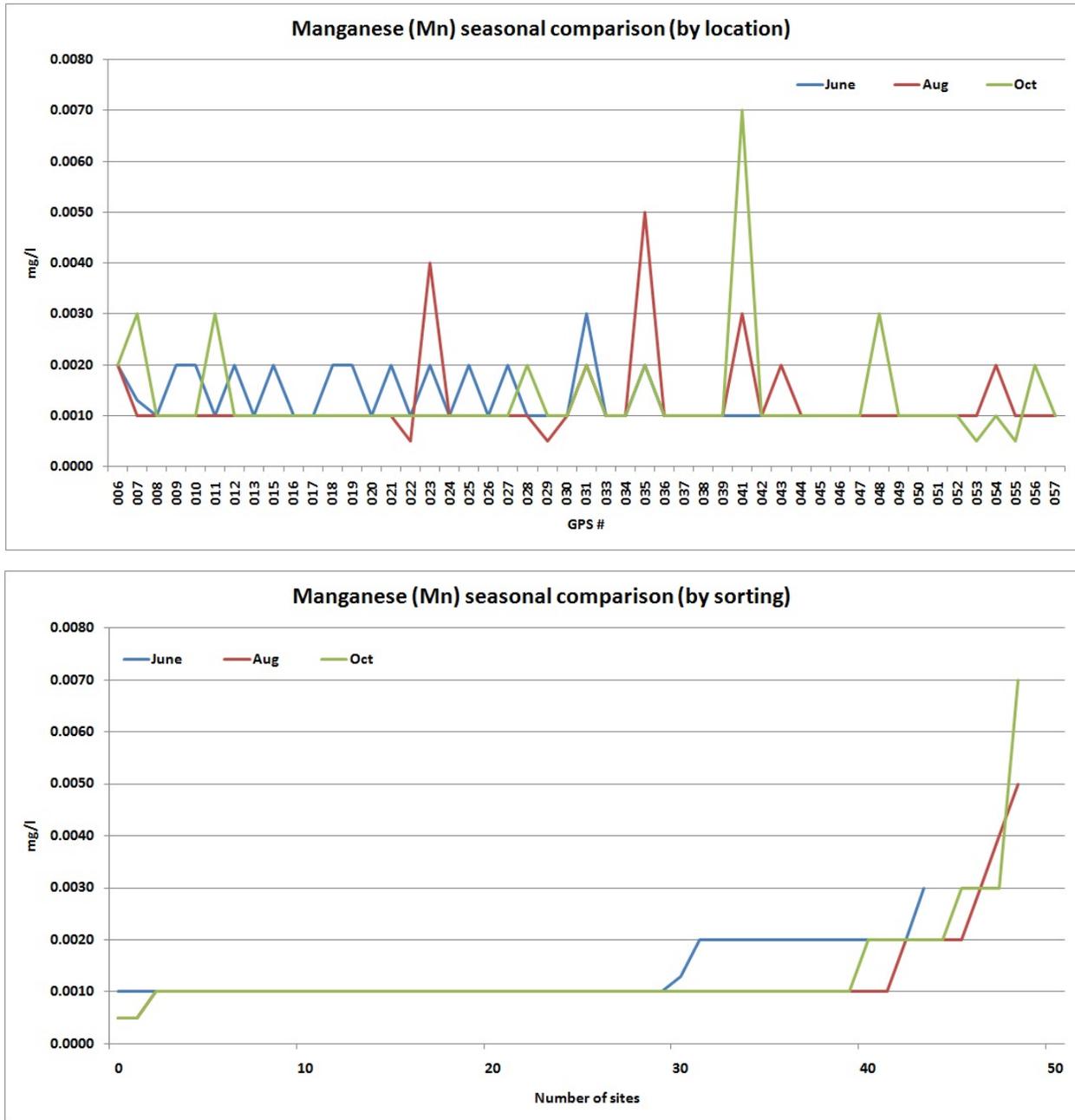


Figure 44. Manganese seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

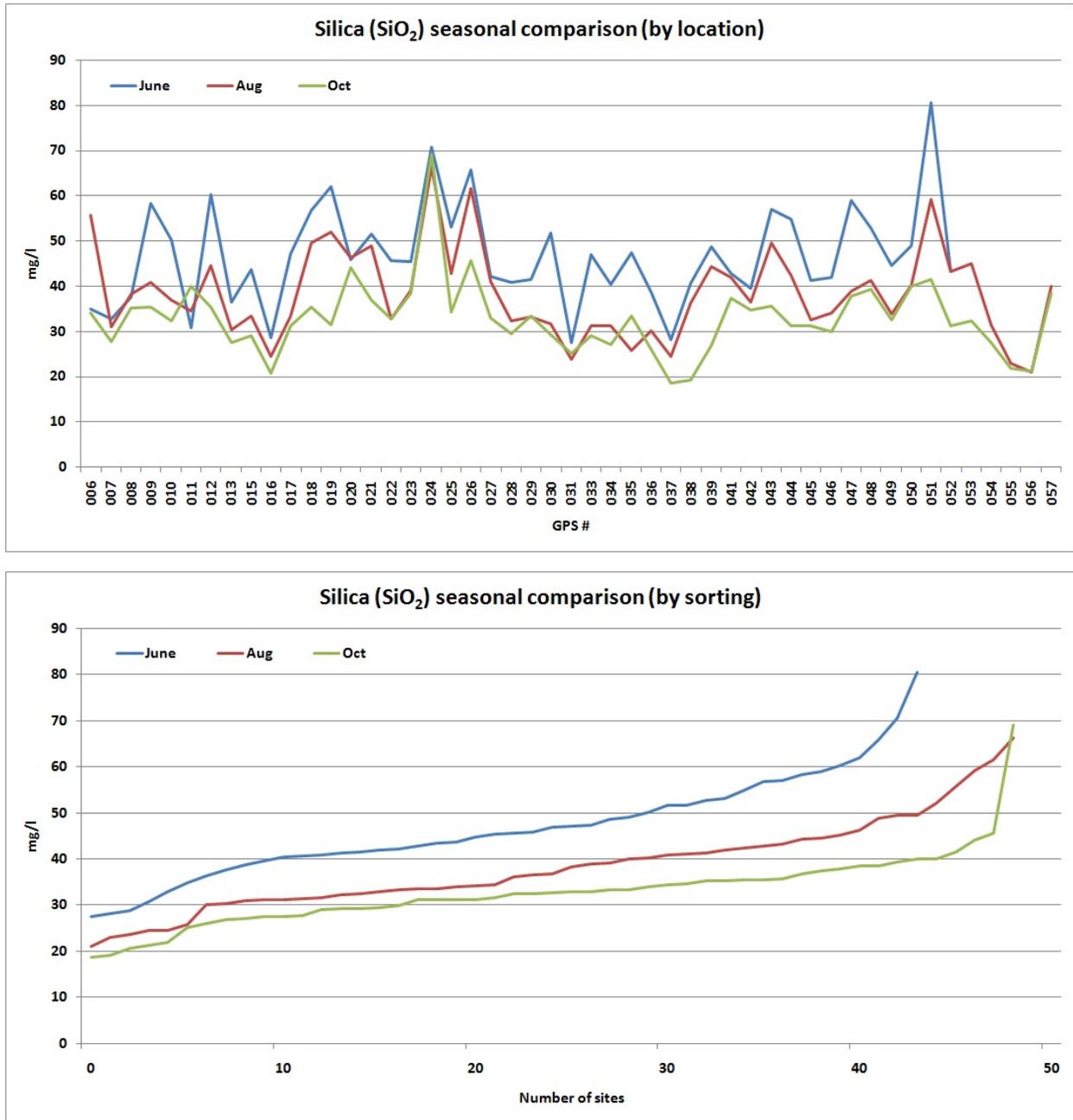


Figure 45. Silica seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

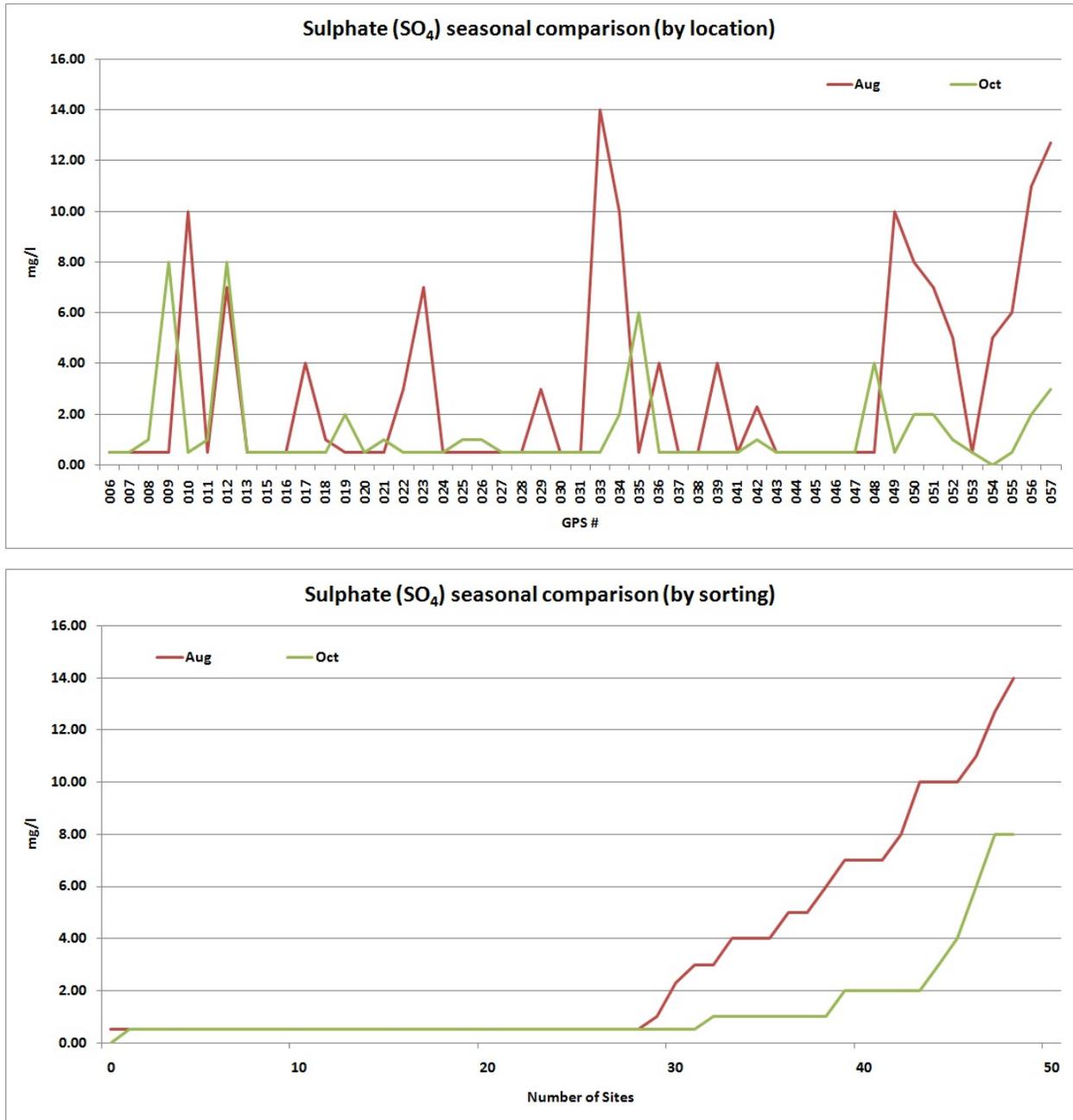


Figure 46. Sulphate seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

Field Tests

Water pH results (Figure 47) are reasonably consistent despite the varied amounts of precipitation during the sampling campaigns. Only one site (station #038) has a value below 7.0, whereas the rest of the results are neutral to slightly alkaline. The sorted results show that values change little between seasons.

Conductivity and TDS (Figure 49) also show little seasonal variation. Patterns are well correlated and although very close, display slight increases from June to October. Considering the high water levels and changeable conditions during the study, the overall reproducibility of the results is surprising.

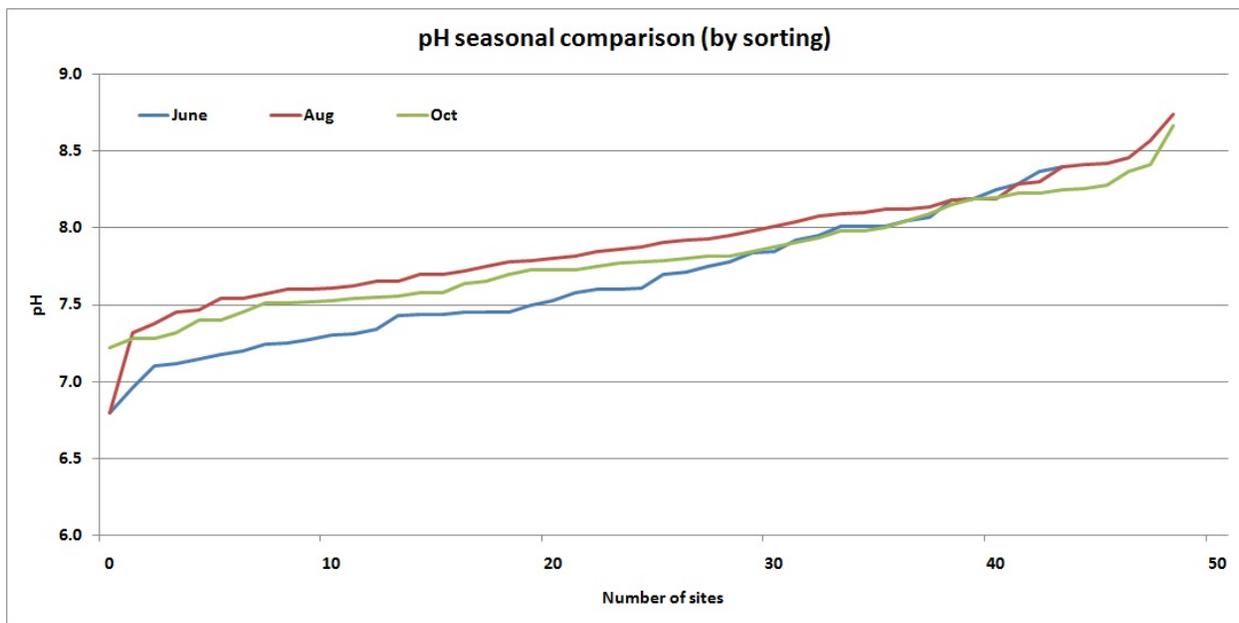
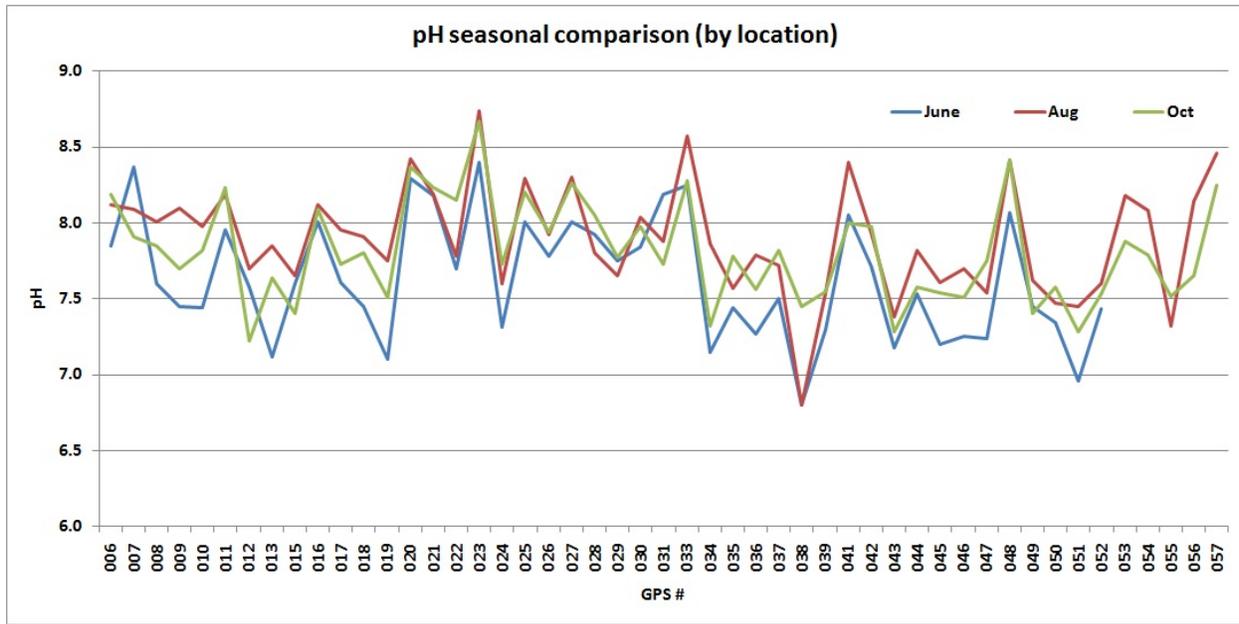


Figure 47. pH seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

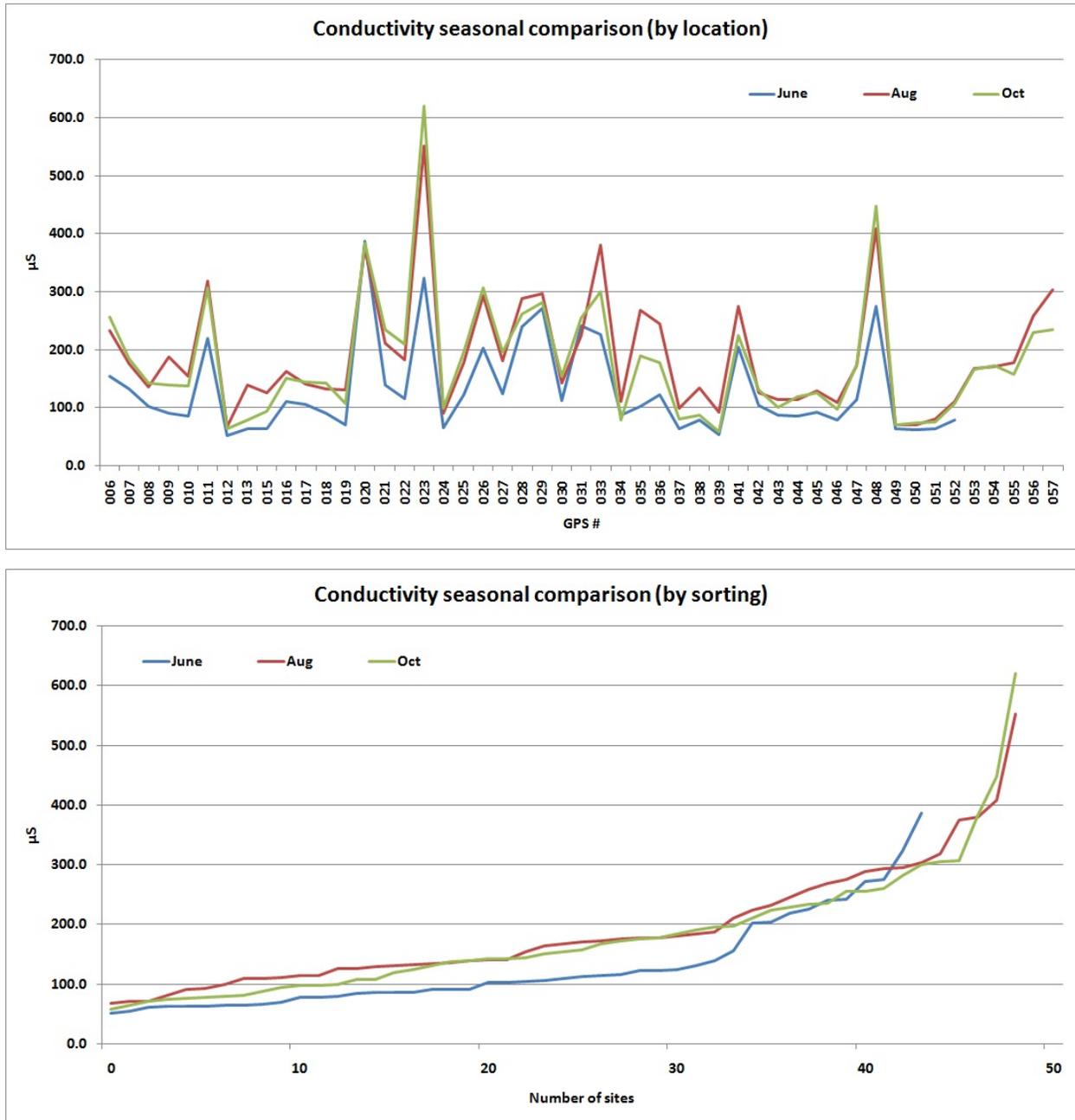


Figure 48. Conductivity seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

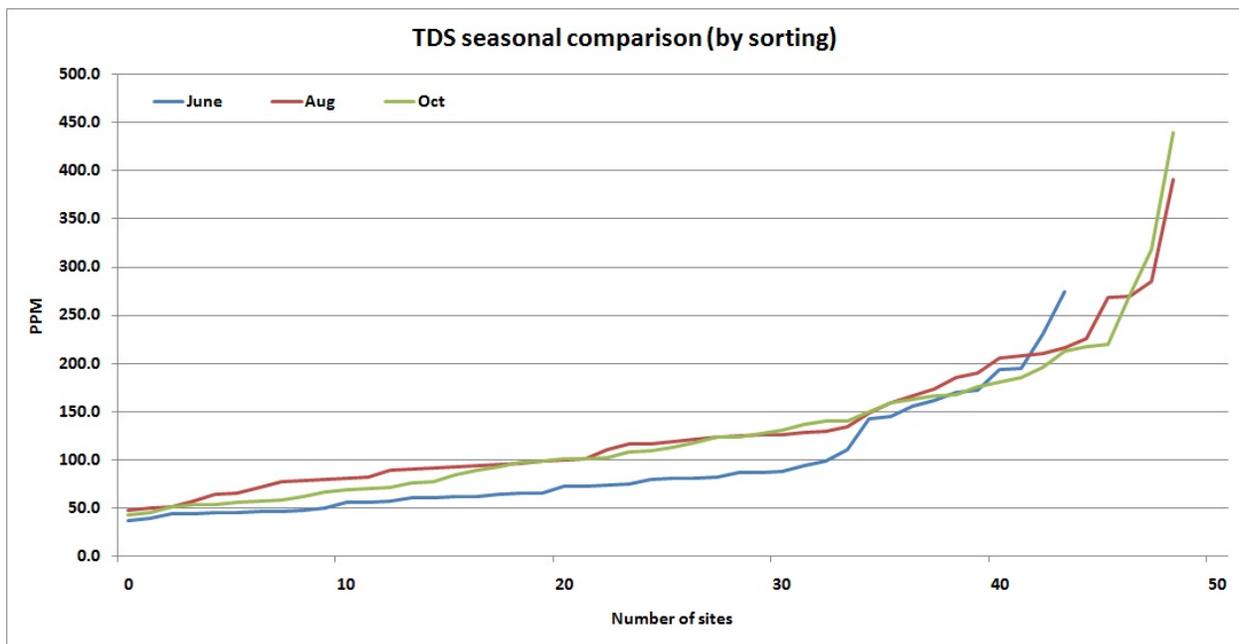
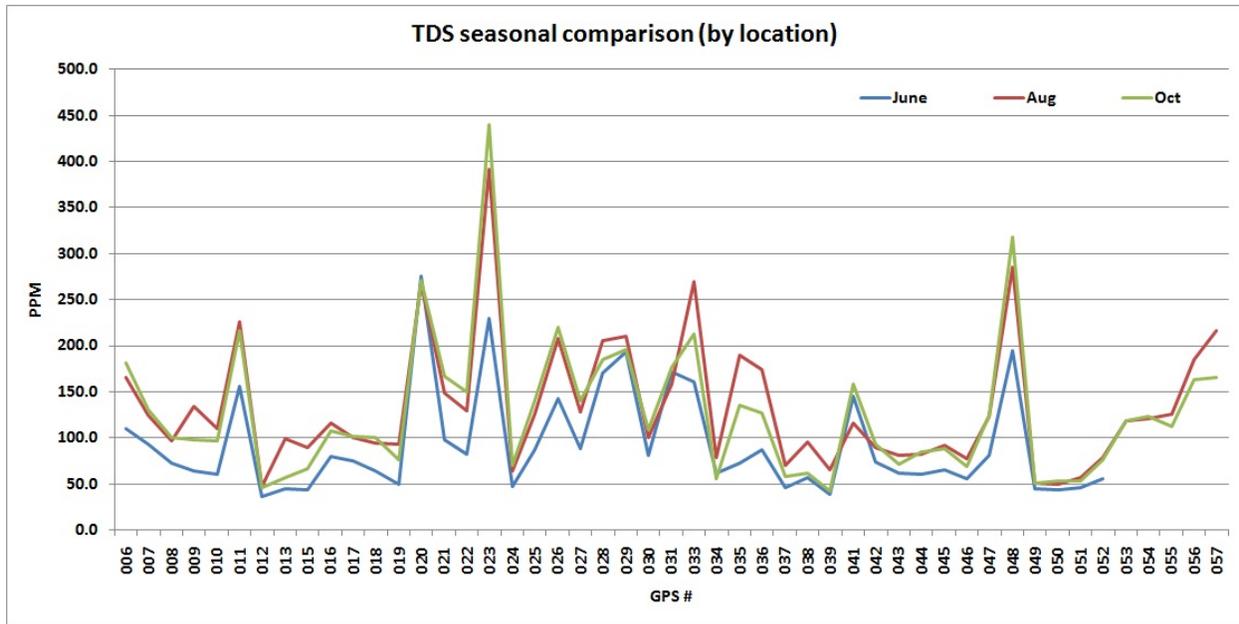


Figure 49. Total dissolved solids seasonal comparison by location (top) and seasonal comparison by sorting by increasing concentration (bottom).

Turbidity

As mentioned previously in the analytical methods section, high turbidity readings can affect the photometer results for some analytes by producing artificially high values. Overestimation of concentrations is caused by the darker colour of the sample (Figure 51) that can interfere with the normal reagent colours.

In the June survey, many samples were found to have high turbidity readings. Figure 50 shows an example of turbid samples that have been stored at the laboratory for two months. The sample bottles do not show suspended particles (colloids) that are clearly settled at the bottom. Instead the coloured solutions show that colloids remain in suspension even after storage for two months.



Figure 50. An example of samples with suspended particles (colloids) that are too fine to be removed by 0.45 micron filtration.

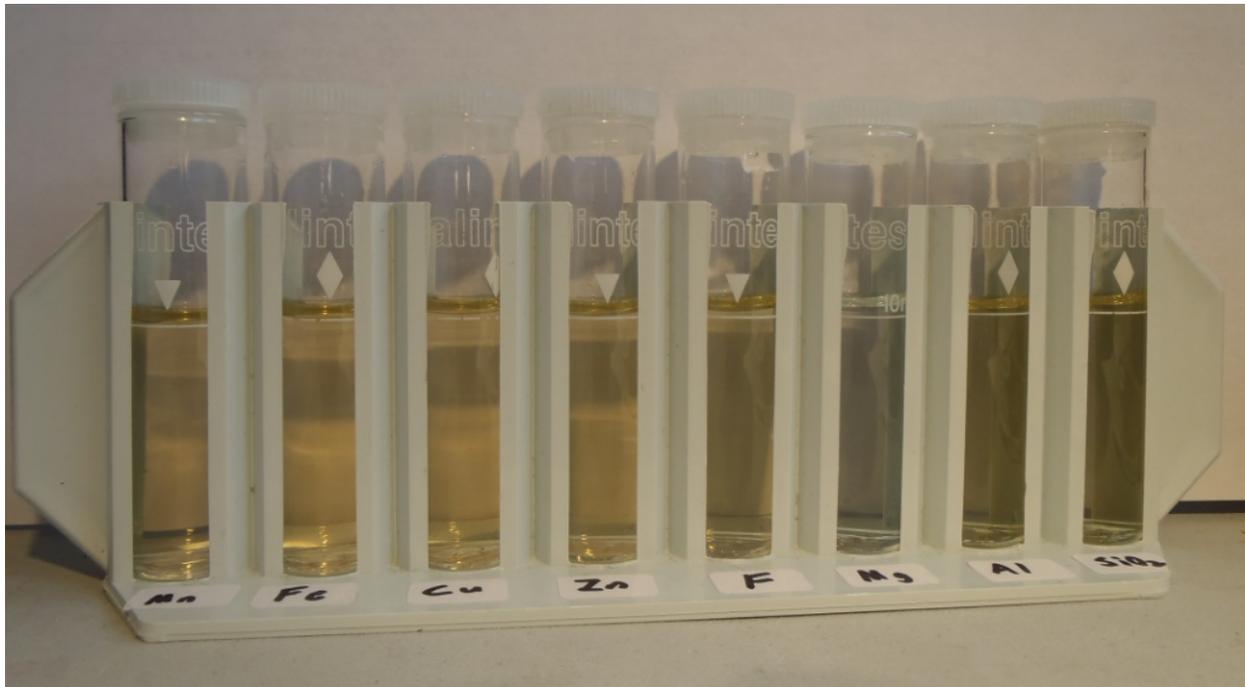


Figure 51. Sample tubes ready for reading. Note the Mg test (third from the right) has a 1x10 dilution requirement, and therefore is not as turbid.

As noted in the discussion of seasonal variation, some analytes are more susceptible to seasonal and daily variations than others; results can be affected by weathering caused by increased run-off and not necessarily be caused by the turbidity effect. Reagents that did not involve a colour test at close to detection limits, such as Cu, MoO_4 , and SO_4 , appeared to be affected by the higher turbidity levels. Elevated turbidity values could introduce a high bias to measured concentrations since the photometer measures an analyte from the intensity of light passing through a solution.

To examine these effects, and validate results, the photometer readings were analyzed for turbidity by: a) plotting against June results, and comparing the result to its laboratory equivalent, b) plotting contours maps; and c) re-analysing the first August samples batch with the method for cancelling turbidity effects outlined in the Photometer section on page 24.

Comparison of analytes versus turbidity and between the photometer (transmittance) and laboratory inductively coupled plasma optical emission spectrometry (ICP-OES) results is a good way to test for measurement issues. ICP-OES is not affected by turbidity since the method involves acid digestion and spectrophotometry, while photometer methodology involves chemical reagents interactions which are then measured at a specific wavelength. Therefore, any light interference caused by turbidity is highlighted by the ICP-OES comparison, as shown in the charts below. This is not a comparison between the methodologies and validation of which one is better, but only a method of identifying potential turbidity causing false positives in the photometer results.

June Concentrations Vs. Turbidity

The tests that have sufficient data for analysis are charted below (Figure 52 to Figure 59). They are divided into two groups: a) analytes where both photometer and laboratory (ICP-OES) trends match; and b) analytes with poor reproducibility between methods.

The first three analytes: Al (Figure 52), ionic Cu (Figure 53) and total Cu (Figure 54), show positive correlations with turbidity for both field and laboratory determinations, thus raising the question of how important the turbidity effect is on the results. This warrants further investigation.

Potassium (Figure 55) shows no changes in response to increasing turbidity. Interestingly, the higher concentrations correspond to lower turbidity levels; an indication that turbidity is not influencing K concentration.

Of note for hardness (Figure 56) and Mg (Figure 57), are their reversed elevated values at turbidity values of between 0 and 20 FTU, and consistently lower values at higher FTU. At lower turbidity water concentration has higher hardness and Mg content, demonstrating further the groundwater origins of these two analytes.

For MoO_4 (Figure 58) and Ni (Figure 59), opposite relationships between the photometer and laboratory are observed. This is a clear example of the turbidity effect on the photometer readings. For MoO_4 there may be some doubt as it is a stable compound compared to Mo, and therefore may be more affected by weathering and turbidity. Regardless, these results raise concerns that warranted further investigation.

Mn results are unaffected by turbidity especially above a detection limit concentration of 0.001 mg/l. The blue Mn colour complex (Figure 6) is visibly more intense at higher Mn concentrations, indicating that photometer Mn analyses are reliable.

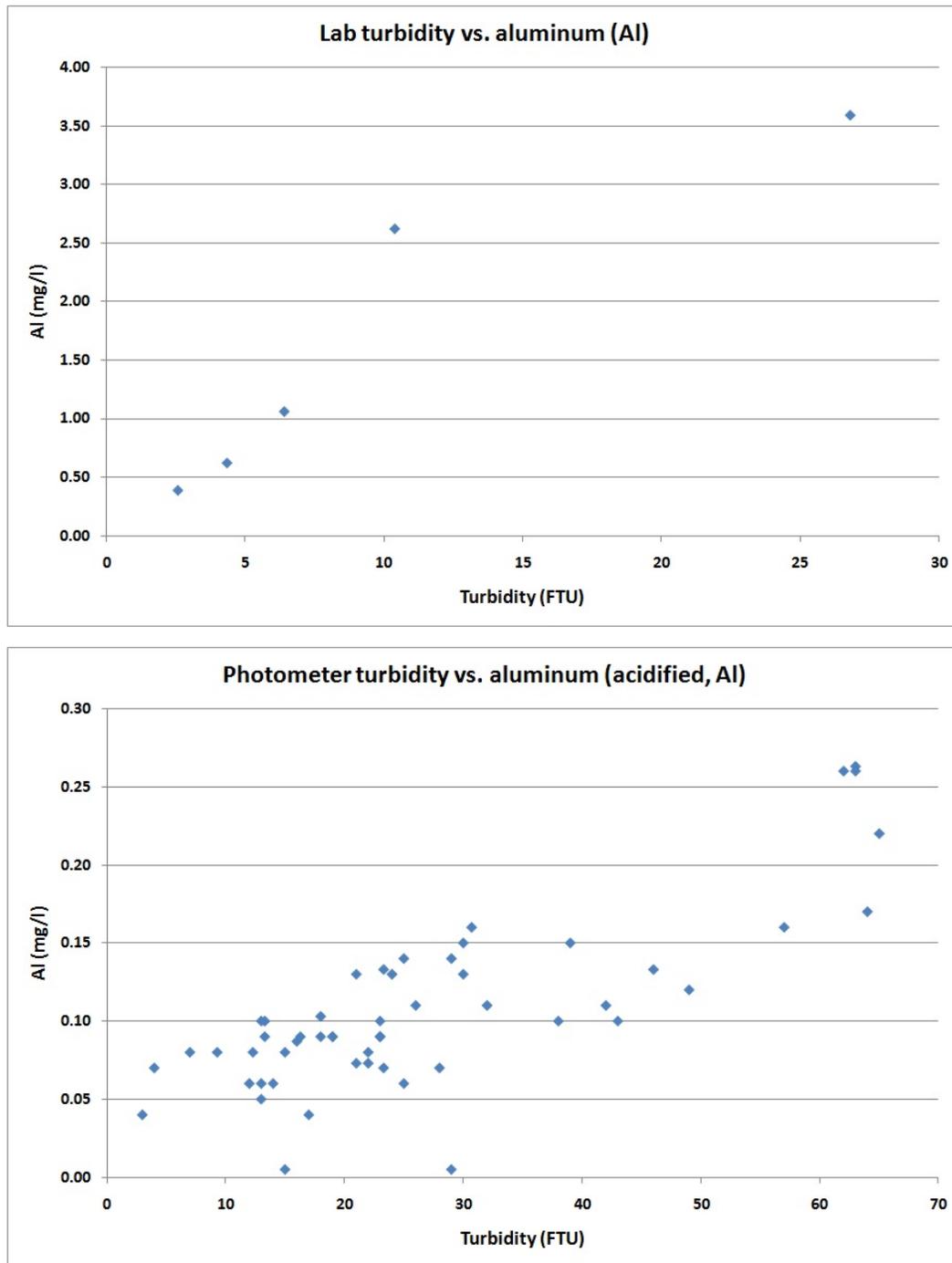


Figure 52. Aluminum concentrations versus turbidity.

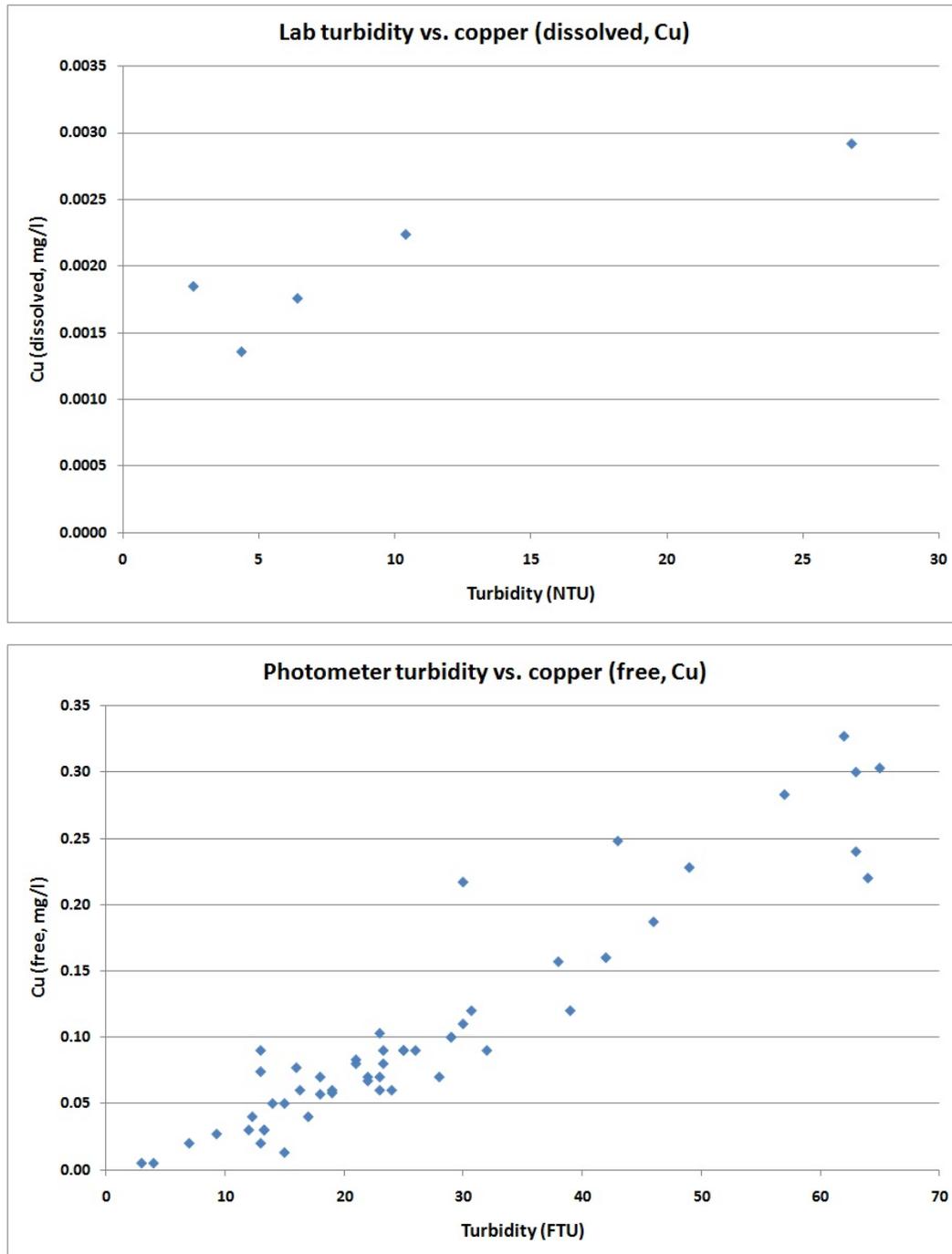


Figure 53. Copper (ionic) concentrations versus turbidity.

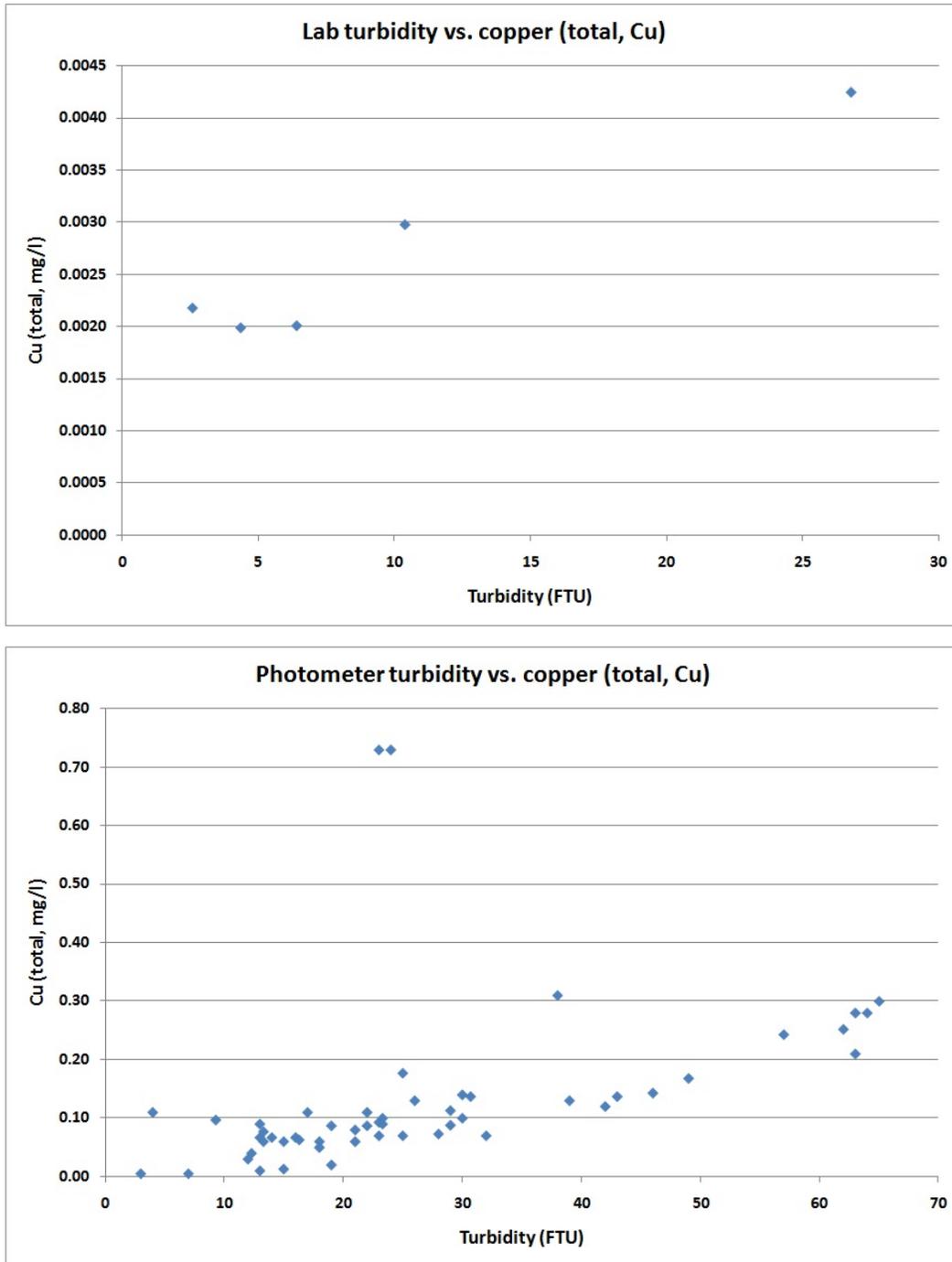


Figure 54. Copper (total) concentrations versus turbidity.

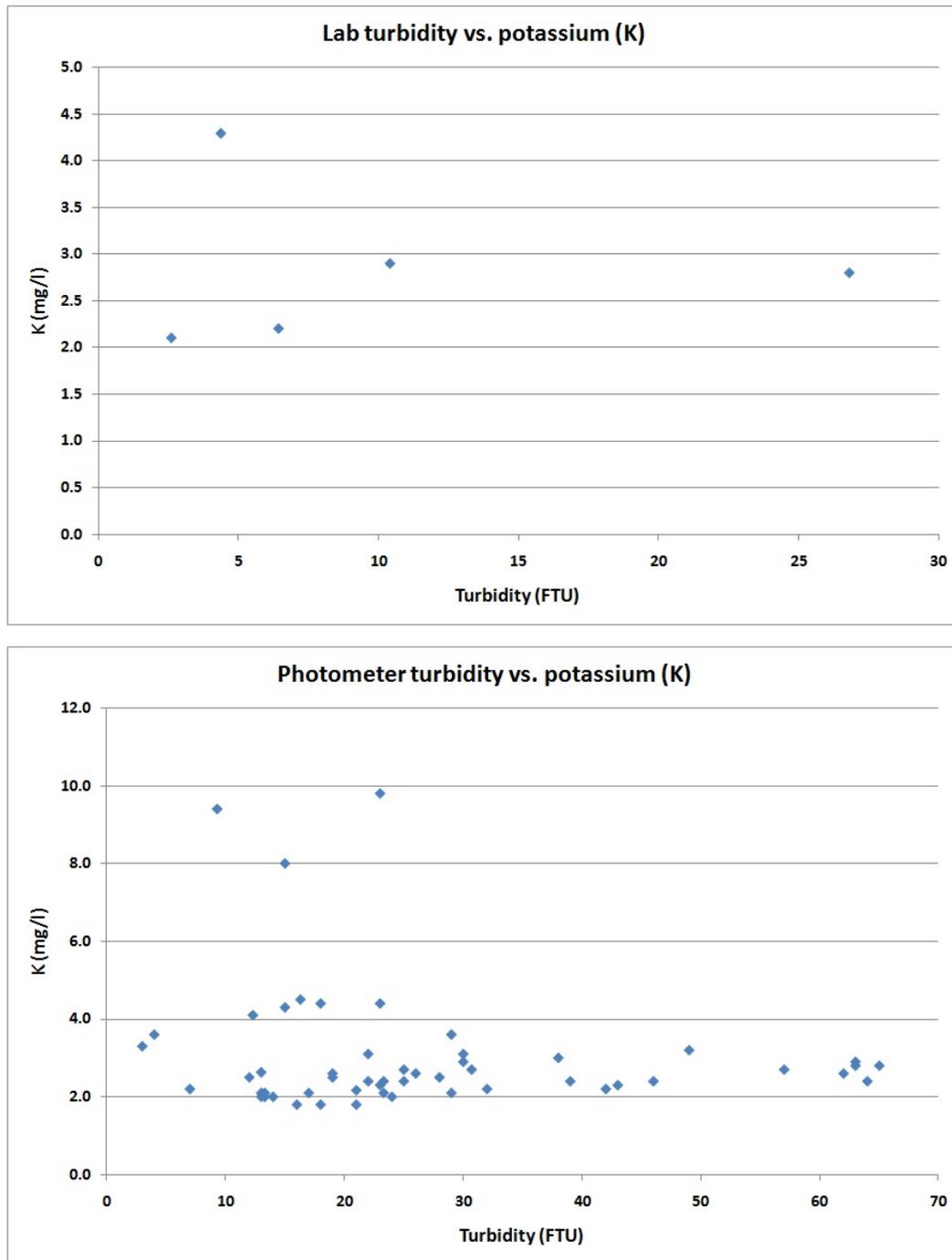


Figure 55. Potassium concentrations versus turbidity.

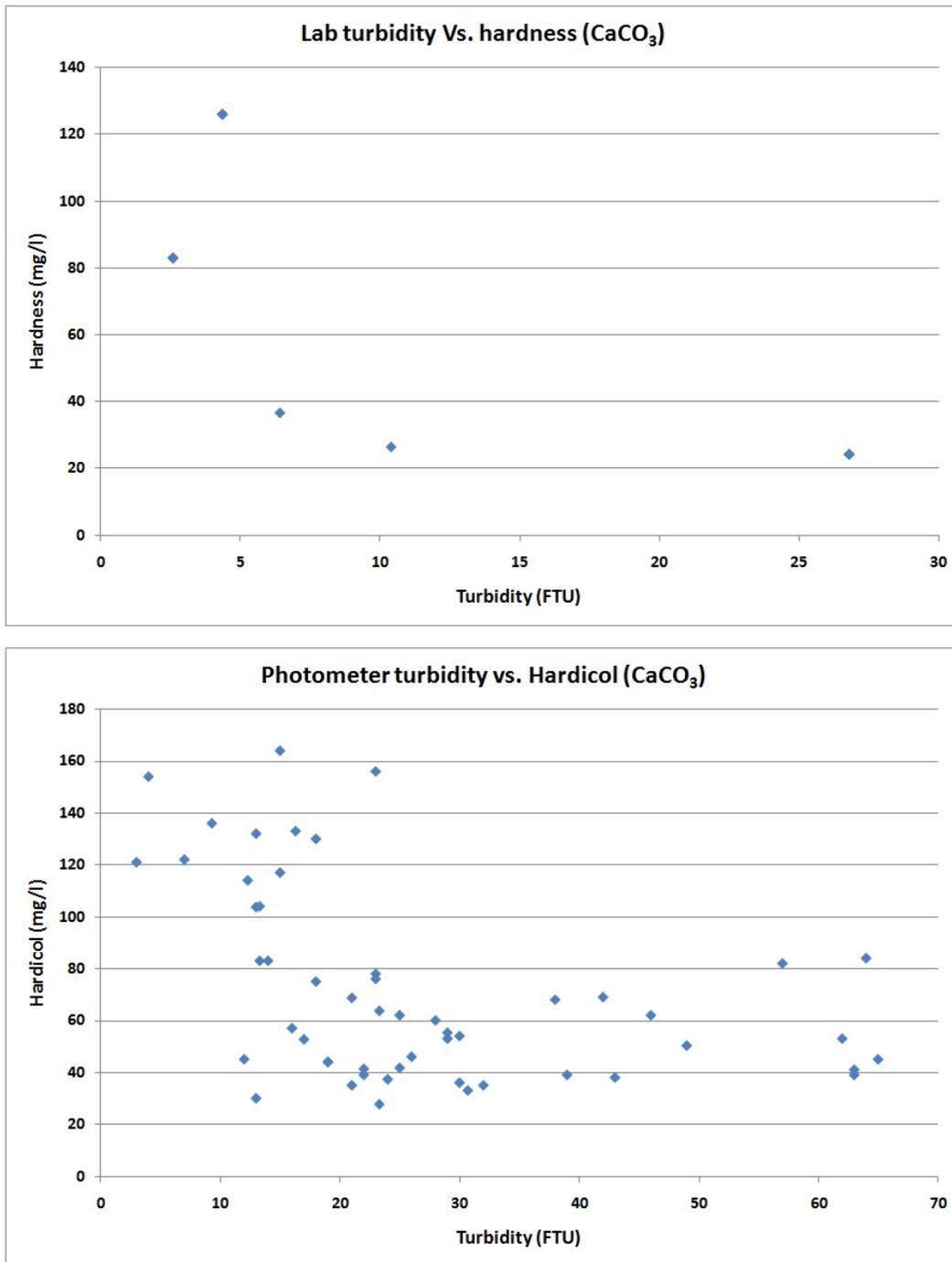


Figure 56. Hardness concentrations versus turbidity.

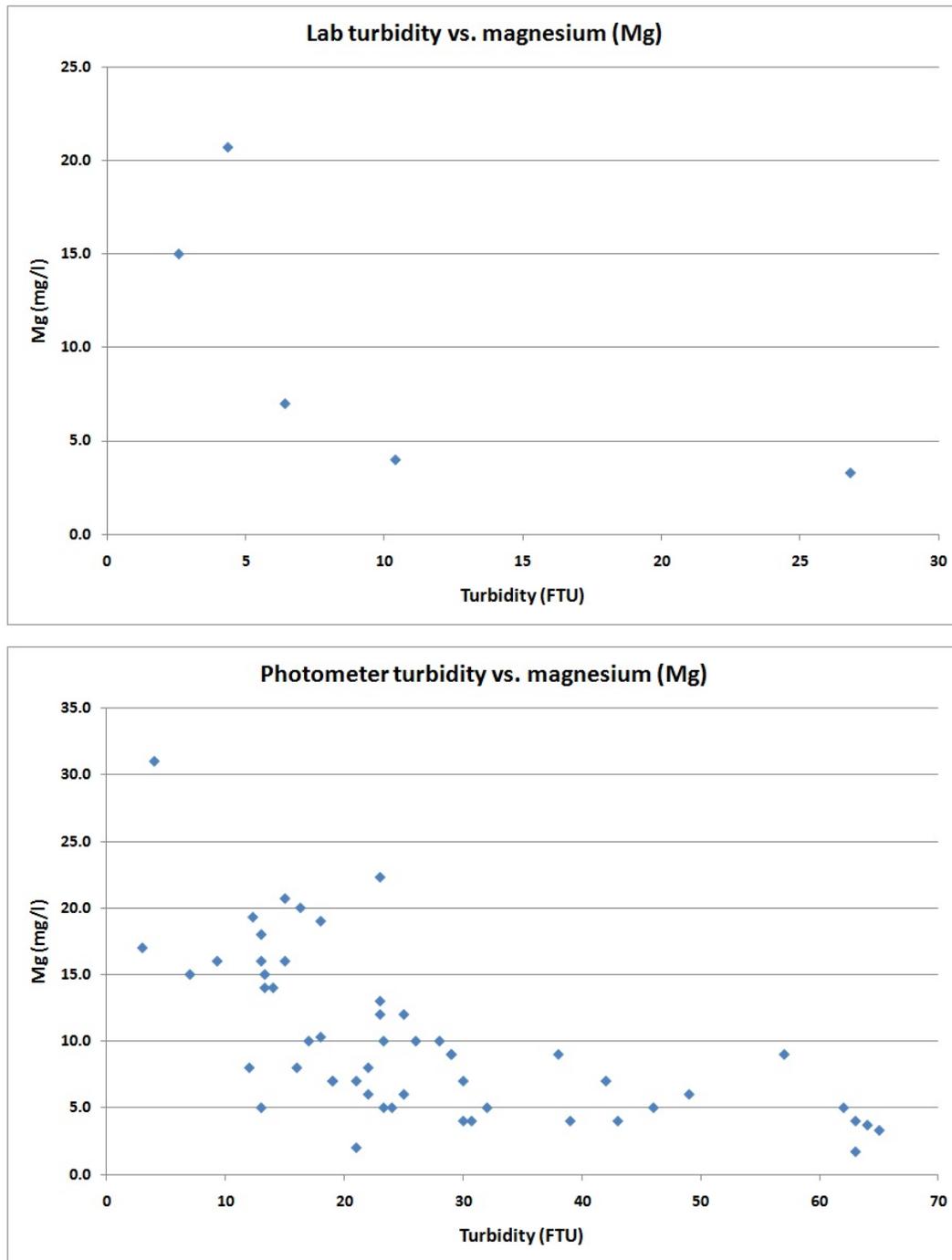


Figure 57. Magnesium concentrations versus turbidity.

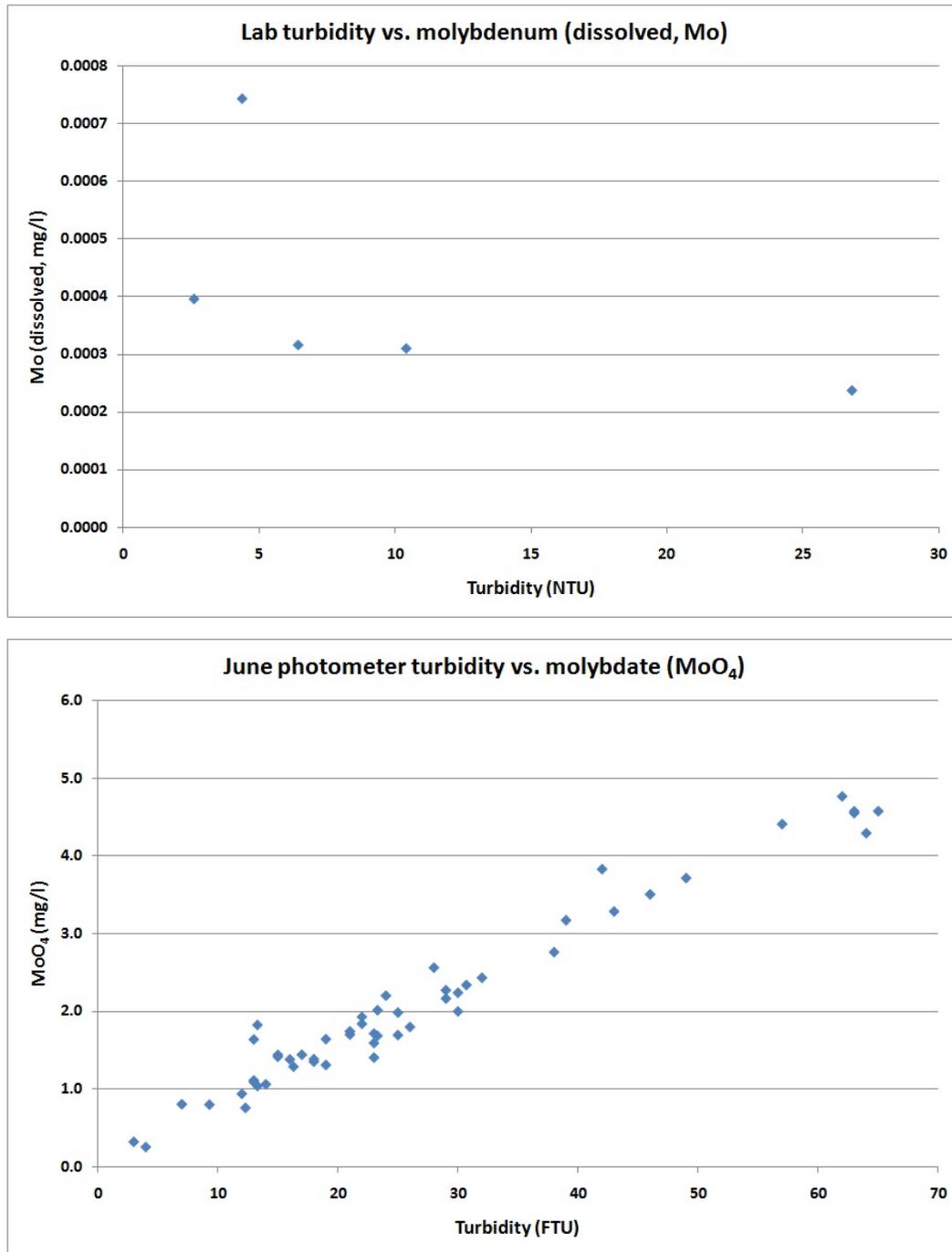


Figure 58. Molybdenum and molybdate concentrations versus turbidity.

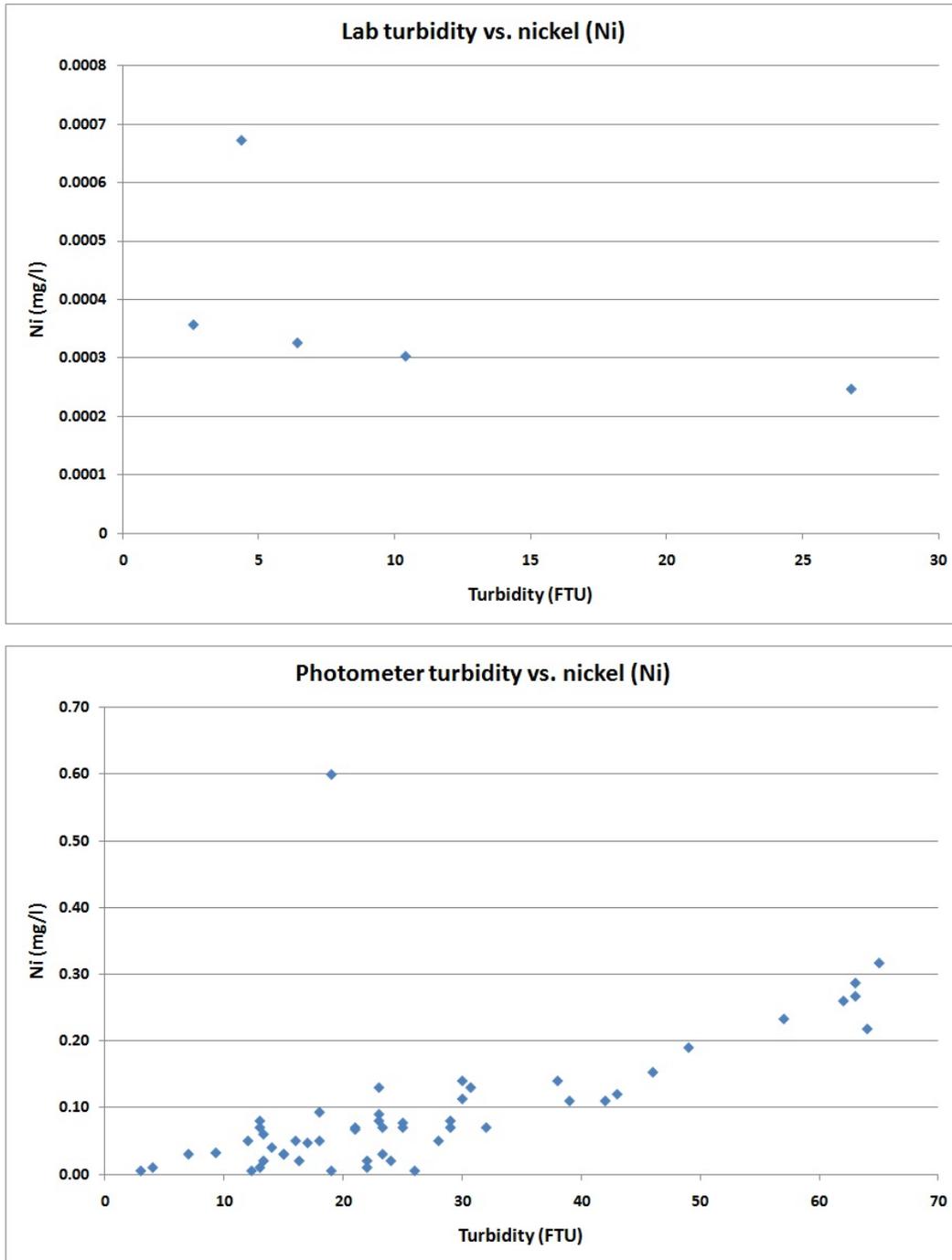


Figure 59. Nickel concentrations versus turbidity.

The second method to examine the relationship between analyte concentrations and turbidity is mapping the photometer results using concentration contours on regional scale maps (Figure 60). The similarity of some of the charts for turbidity raises the questions of other possible influences on the results, such as terrain and geology.

Since the analyte versus turbidity charts and contour plots do not conclusively determine the effect of turbidity on the photometer measurements, a third test was devised in August for the first batch of field samples. The test covered all the analytes that may have been influenced by turbidity. It consisted of running a photometer test with the June procedures, using a filtered deionized water blank, and a second test on the same sample with the Palintest recommended procedures (discussed on page 24) using a filtered blank. The results are outlined in Table 5 and show a distinct turbidity influence on the photometer readings. All of the tests with the new procedure registered below detection limit results, except for one Cu total and two SO₄ tests. This is in sharp contrast to the previous original tests that produced values for all the analytes results except for one ionic Cu free and five Ni results.

Due to the obvious effect of turbidity, usage of filtered water blanks was implemented for the rest of the study, and the deionized water blank was used only in measuring the overall turbidity FTU readings for each sample.

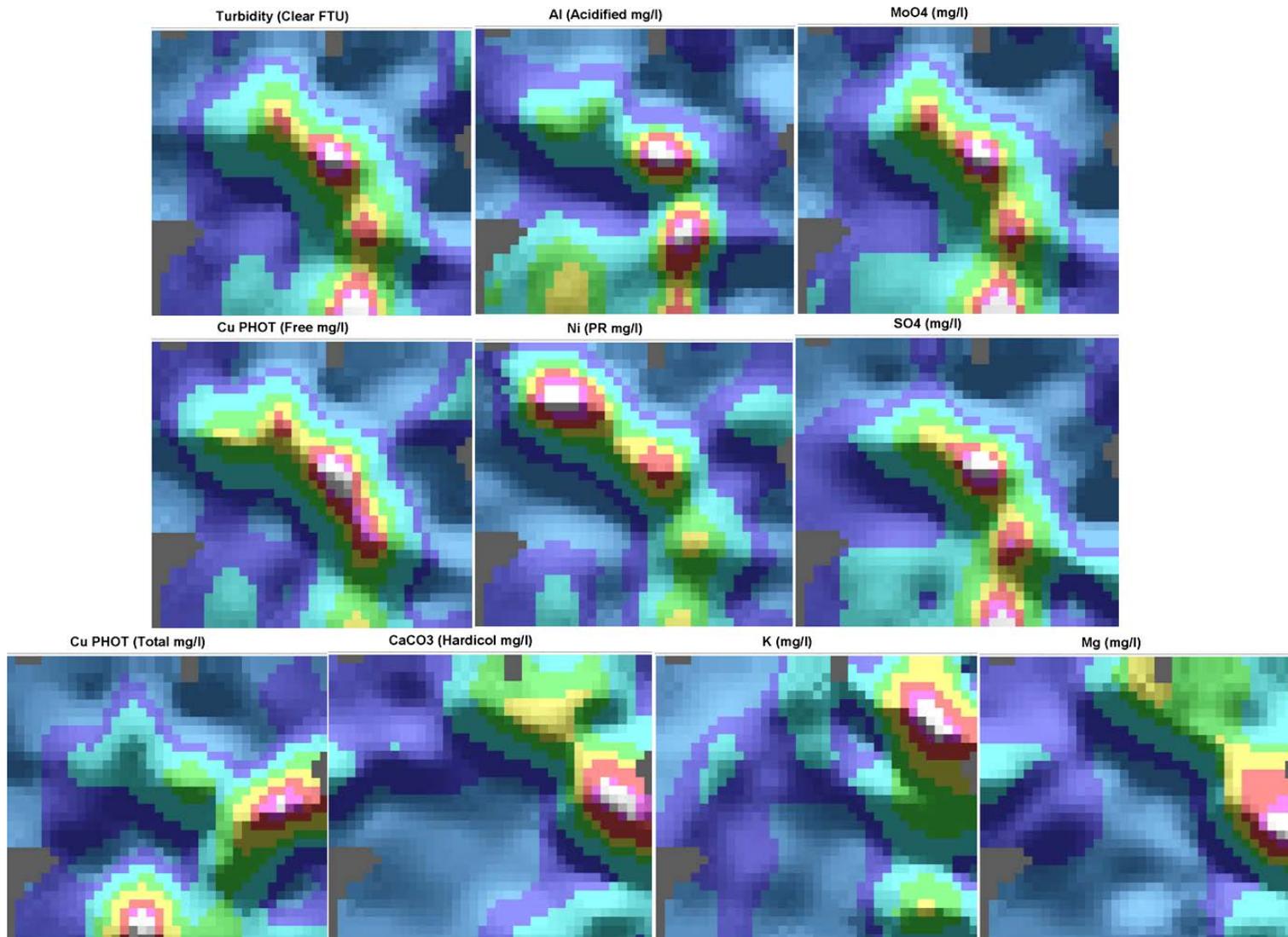


Figure 60. Collection of gridded images showing the June relationship between analytes and turbidity. Gridded maps boxes equal NTS 093B/13.

Table 5. Rerun of photometer analysis with filtered blanks analysis. Refer to page 24 for description of blank types.

SAMPLE ID	Blank Type	Turbidity (FTU)	Cu PHOT (Free, mg/l)	Cu PHOT (Total, mg/l)	MoO ₄ (mg/l)	Ni (PR, mg/l)	SO ₄ (mg/l)
L160821030081	Deionized	11.3	0.040	0.070	0.861	0.020	7.0
L160821030081	Filtered	2.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160803500084	Deionized	3.3	0.010	0.020	0.443	<0.005	1.0
L160803500084	Filtered	<0.5	<0.005	0.013	<0.005	<0.005	<0.5
L160897220085	Deionized	12.0	0.030	0.107	0.900	0.033	6.0
L160897220085	Filtered	2.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160836400086	Deionized	11.0	0.030	0.043	0.870	<0.005	6.0
L160836400086	Filtered	3.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160881010087	Deionized	10.0	<0.005	0.017	0.877	<0.005	6.0
L160881010087	Filtered	3.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160899520088	Deionized	13.0	0.060	0.060	0.933	<0.005	6.0
L160899520088	Filtered	3.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160803650089	Deionized	14.0	0.050	0.050	1.150	0.040	7.0
L160803650089	Filtered	1.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160872490090	Deionized	25.0	0.070	0.048	1.547	<0.005	9.0
L160872490090	Filtered	2.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160885920091	Deionized	22.0	0.070	0.050	1.563	0.030	9.0
L160885920091	Filtered	2.0	<0.005	<0.005	<0.005	<0.005	<0.5
L160885924092	Deionized	27.0	0.100	0.090	2.070	0.110	14.0
L160885924092	Filtered	5.0	<0.005	<0.005	<0.005	<0.005	4.0
L160885924093	Deionized	27.0	0.110	0.107	1.973	0.080	14.0
L160885924093	Filtered	5.0	<0.005	<0.005	<0.005	<0.005	4.0

Results

Orientation Survey Results

A small orientation survey was carried out in June close to Vancouver. Its purpose was to determine the best field sample collection procedures. Detailed results are shown in Table 6 and Table 7. Additional details such as locations and dates are available in the Digital Appendix. Results from the photometer tests were inconclusive at defining a single preferred method for routine sample collection. This was due mainly to the small sample set and lower-than-expected analyte concentrations at most sites.

Table 6. Results from June orientation survey.

SAMPLE ID	Type	Field pH	Analysis pH	Lab pH	Field Cond. (µS)	Analysis Cond.	Lab Cond. (µS)	Field TDS (ppm)	Analysis TDS	Lab TDS (ppm)	Turbidity (FTU)	Comments
L160658700001	Unfiltered-unacidified	6.80	6.80	6.84	13.0	18.8 µS	13.5	9.3	13.6 ppm	19	1	Lynn Valley
L160658700002	Unfiltered-acidified	6.80	1.56	6.84	13.0	12.94 ms	13.5	9.3	9.16 ppt	19	0.5	Lynn Valley
L160658700003	Filtered-unacidified	6.80	6.97	6.84	13.0	14.4 µS	13.5	9.3	10.2 ppm	19	0.5	Lynn Valley
L160658700004	Filtered-acidified	6.80	1.62	6.84	13.0	12.7 ms	13.5	9.3	9.02 ppt	19	0.5	Lynn Valley
L160682130005	Unfiltered-unacidified	6.91	6.79	7.50	78.5	74.5 µS	79.9	55.8	52.8 ppm	48	3.3	Fraserview
L160682130006	Unfiltered-acidified	6.91	1.66	7.50	78.5	12.41 ms	79.9	55.8	8.80 ppt	48	0.5	Fraserview
L160682130007	Filtered-unacidified	6.91	6.75	7.50	78.5	78.5 µS	79.9	55.8	53.7 ppm	48	0.5	Fraserview
L160682130008	Filtered-acidified	6.91	1.61	7.50	78.5	12.56 ms	79.9	55.8	8.87 ppt	48	0.5	Fraserview
L160600000011	Unfiltered-unacidified	7.70	7.36	6.97	17.0	16.3 µS	16.5	12.1	11.8 ppm	15	0.5	Britannia Creek
L160600000012	Unfiltered-acidified	7.70	1.96	6.97	17.0	12.44 ms	16.5	12.1	8.84 ppt	15	0.5	Britannia Creek
L160600000013	Filtered-unacidified	7.70	7.44	6.97	17.0	16.9 µS	16.5	12.1	12.1 ppm	15	1.0	Britannia Creek
L160600000014	Filtered-acidified	7.70	2.16	6.97	17.0	12.27 ms	16.5	12.1	8.18 ppt	15	0.5	Britannia Creek
L160600000015	Unfiltered-unacidified	7.50	7.28	6.93	14.6	14.1 µS	14.1	10.3	10.1 ppm	10	0.5	Furry Creek
L160600000016	Unfiltered-acidified	7.50	1.83	6.93	14.6	11.3 ms	14.1	10.3	8.00 ppt	10	0.5	Furry Creek
L160600000017	Filtered-unacidified	7.50	7.36	6.93	14.6	13.6 µS	14.1	10.3	9.9 ppm	10	0.5	Furry Creek
L160600000018	Filtered-acidified	7.50	1.87	6.93	14.6	11.32 ms	14.1	10.3	8.03 ppt	10	0.5	Furry Creek
L160600000009	Deionized	NA	5.84		NA	2.8 µS		NA	2.0 ppm		0.5	
L160600000010	Standard	NA	1.94		NA	4.42 ms		NA	3.0 ppt		0.5	
		Al (mg/l)	Lab Al (mg/l)	CaCO ₃ (Calcol, mg/l)	PHOT Ca (mg/l) 0.4 conversion	Lab Ca (mg/l)	CaCO ₃ (Hardicol, mg/l)	Lab Hardness (CaCO ₃ , mg/l)	Cl ⁻ (mg/l)	Lab Cl ⁻ (mg/l)		Comments
L160658700001	Unfiltered-unacidified	0.010	0.0383	6.0	2.40	1.54	8.0	4.76	0.90	0.5		Lynn Valley
L160658700002	Unfiltered-acidified	0.110	0.0383	500			2.5	4.76	0.57	0.5		Lynn Valley
L160658700003	Filtered-unacidified	0.010	0.0383	6.0	2.40	1.54	10.0	4.76	0.60	0.5		Lynn Valley
L160658700004	Filtered-acidified	0.090	0.0383	500			2.5	4.76	0.10	0.5		Lynn Valley
L160682130005	Unfiltered-unacidified	0.010	0.0633	9.0	3.60	6.84	17.0	19.9	3.90	4.43		Fraserview
L160682130006	Unfiltered-acidified	0.130	0.0633	500			2.5	19.9	11.70	4.43		Fraserview
L160682130007	Filtered-unacidified	0.010	0.0633	5.0	2.00	6.84	28.0	19.9	5.37	4.43		Fraserview
L160682130008	Filtered-acidified	0.080	0.0633	500			2.5	19.9	5.10	4.43		Fraserview
L160600000011	Unfiltered-unacidified	0.010	0.0568	6.0	2.40	2.30	11.3	6.64	0.60	0.5		Britannia Creek
L160600000012	Unfiltered-acidified	0.100	0.0568	500			2.5	6.64	0.30	0.5		Britannia Creek
L160600000013	Filtered-unacidified	0.010	0.0568	6.0	2.40	2.30	7.0	6.64	3.57	0.5		Britannia Creek
L160600000014	Filtered-acidified	0.080	0.0568	500			2.5	6.64	0.40	0.5		Britannia Creek
L160600000015	Unfiltered-unacidified	0.010	0.0572	6.0	2.40	1.87	7.0	5.43	0.20	0.5		Furry Creek
L160600000016	Unfiltered-acidified	0.010	0.0572	500			2.5	5.43	4.40	0.5		Furry Creek
L160600000017	Filtered-unacidified	0.010	0.0572	6.0	2.40	1.87	5.0	5.43	4.40	0.5		Furry Creek
L160600000018	Filtered-acidified	0.080	0.0572	500			2.5	5.43	0.30	0.5		Furry Creek
L160600000009	Deionized	0.010		6.0			3.0		0.60			
L160600000010	Standard	0.040		500			2.5		7.07			

Table 7. Results from June orientation survey, continued. Additional details are available in Digital Appendix.

		Cu PHOT (Total, mg/l)	Cu Lab (Total, mg/l)	F ⁻ (mg/l)	Lab F ⁻ (mg/l)	Fe (mg/l)	Lab Fe (mg/l)	K (mg/l)	Lab K (mg/l)	Mg (mg/l)	Lab Mg (mg/l)	Mn (mg/l)	Lab Mn (mg/l)	Comments
L160658700001	Unfiltered-unacidified	0.050	0.0005	0.317	0.02	0.010	0.012	0.20	0.126	3.0	0.22	0.0010	0.00056	Lynn Valley
L160658700002	Unfiltered-acidified	0.810	0.0005	0.450	0.02	0.010	0.012	0.50	0.126	3.0	0.22	0.00083	0.00056	Lynn Valley
L160658700003	Filtered-unacidified	0.010	0.0005	0.345	0.02	0.020	0.012	2.00	0.126	2.0	0.22	0.0010	0.00056	Lynn Valley
L160658700004	Filtered-acidified	0.996	0.0005	0.387	0.02	0.020	0.012	0.20	0.126	2.0	0.22	0.00083	0.00056	Lynn Valley
L160682130005	Unfiltered-unacidified	0.060	0.00413	0.617	0.04	0.040	0.105	4.60	0.874	4.0	0.68	0.0040	0.01310	Fraserview
L160682130006	Unfiltered-acidified	1.092	0.00413	0.690	0.04	0.040	0.105	3.90	0.874	2.0	0.68	0.00083	0.01310	Fraserview
L160682130007	Filtered-unacidified	0.040	0.00413	0.467	0.04	0.020	0.105	3.80	0.874	1.0	0.68	0.0030	0.01310	Fraserview
L160682130008	Filtered-acidified	0.976	0.00413	0.750	0.04	0.040	0.105	4.10	0.874	2.0	0.68	0.00083	0.01310	Fraserview
L160600000011	Unfiltered-unacidified	0.010	0.00856	0.280	0.02	0.010	0.028	0.60	0.05	1.0	0.20	0.0010	0.00156	Britannia Creek
L160600000012	Unfiltered-acidified	0.328	0.00856	0.533	0.02	0.050	0.028	4.80	0.05	1.0	0.20	0.00083	0.00156	Britannia Creek
L160600000013	Filtered-unacidified	0.010	0.00856	0.287	0.02	0.050	0.028	0.37	0.05	0.5	0.20	0.0050	0.00156	Britannia Creek
L160600000014	Filtered-acidified	1.160	0.00856	0.470	0.02	0.020	0.028	0.1	0.05	1.0	0.20	0.00083	0.00156	Britannia Creek
L160600000015	Unfiltered-unacidified	0.030	0.0167	0.300	0.02	0.050	0.014	0.20	0.095	1.0	0.18	0.00083	0.00130	Furry Creek
L160600000016	Unfiltered-acidified	1.500	0.0167	0.500	0.02	0.050	0.014	0.1	0.095	0.0	0.18	0.00083	0.00130	Furry Creek
L160600000017	Filtered-unacidified	0.010	0.0167	0.300	0.02	0.050	0.014	0.50	0.095	0.5	0.18	0.00083	0.00130	Furry Creek
L160600000018	Filtered-acidified	0.963	0.0167	0.370	0.02	0.050	0.014	0.1	0.095	0.5	0.18	0.00083	0.00130	Furry Creek
L160600000009	Deionized	0.010		0.180		0.050		0.1		2.3		0.0010		
L160600000010	Standard	0.840		0.867		0.100		1.20		4.3		0.00083		
		MoO ₃ (mg/l)	PHOT Mo (mg/l) 0.6 conversion	Lab Mo (mg/l)	Ni (mg/l)	Lab Ni (mg/l)	SiO ₂ (mg/l)	Lab SiO ₂ (mg/l)	SO ₄ (mg/l)	Lab SO ₄ (mg/l)	Zn (mg/l)	Zn (EDTA, mg/l)	Lab Zn (mg/l)	Comments
L160658700001	Unfiltered-unacidified	0.030	0.0180	0.000316	0.250	0.0005	3.93	3.27	0.5	1.06	0.008	0.008	0.0030	Lynn Valley
L160658700002	Unfiltered-acidified	0.150	0.0900	0.000316	4.483	0.0005	4.30	3.27	7.0	1.06	0.7000	0.008	0.0030	Lynn Valley
L160658700003	Filtered-unacidified	0.223	0.1338	0.000316	0.250	0.0005	3.93	3.27	3.0	1.06	0.008	0.008	0.0030	Lynn Valley
L160658700004	Filtered-acidified	0.030	0.0180	0.000316	6.273	0.0005	4.50	3.27	14.0	1.06	0.6070	0.008	0.0030	Lynn Valley
L160682130005	Unfiltered-unacidified	0.267	0.1602	0.000333	0.163	0.0005	6.07	4.17	6.0	3.28	0.0333	0.008	0.0067	Fraserview
L160682130006	Unfiltered-acidified	0.143	0.0858	0.000333	2.673	0.0005	6.60	4.17	13.3	3.28	0.6700	0.0300	0.0067	Fraserview
L160682130007	Filtered-unacidified	0.123	0.0738	0.000333	0.250	0.0005	5.60	4.17	4.0	3.28	0.0500	0.0200	0.0067	Fraserview
L160682130008	Filtered-acidified	0.230	0.1380	0.000333	3.910	0.0005	5.40	4.17	6.0	3.28	0.5570	0.008	0.0067	Fraserview
L160600000011	Unfiltered-unacidified	0.043	0.0258	0.000240	0.053	0.0005	4.40	3.22	2.0	1.92	0.0100	0.008	0.0106	Britannia Creek
L160600000012	Unfiltered-acidified	0.070	0.0420	0.000240	2.710	0.0005	3.90	3.22	18.0	1.92	0.6630	0.008	0.0106	Britannia Creek
L160600000013	Filtered-unacidified	0.010	0.0060	0.000240	0.007	0.0005	3.70	3.22	1.0	1.92	0.0100	0.008	0.0106	Britannia Creek
L160600000014	Filtered-acidified	0.010	0.0060	0.000240	4.923	0.0005	4.00	3.22	8.0	1.92	0.6030	0.008	0.0106	Britannia Creek
L160600000015	Unfiltered-unacidified	0.070	0.0420	0.000207	0.250	0.0005	3.70	3.17	2.0	1.44	0.0130	0.008	0.0117	Furry Creek
L160600000016	Unfiltered-acidified	0.100	0.0600	0.000207	2.2000	0.0005	3.90	3.17	29.0	1.44	0.8000	0.008	0.0117	Furry Creek
L160600000017	Filtered-unacidified	0.100	0.0600	0.000207	0.250	0.0005	3.70	3.17	15.0	1.44	0.008	0.008	0.0117	Furry Creek
L160600000018	Filtered-acidified	0.060	0.0360	0.000207	2.6300	0.0005	3.60	3.17	27.0	1.44	0.7670	0.008	0.0117	Furry Creek
L160600000009	Deionized	0.067			0.250		0.30		1.0		0.008			
L160600000010	Standard	0.010			4.850		0.30		19.0		0.7770	0.0500		

Study Area Results

The following maps (Figure 61 to Figure 117) show the results from the photometer and PDV determinations. The maps include only data that is reliable for interpretation. Results are plotted as percentile values of 50%, 75%, 87%, 93%, 98% and 100%. All units are in mg/l unless otherwise indicated. A colour spectrum from red (acid) to blue (alkaline) was used to display pH variation on the maps.

pH

Water pH values (Figure 61 to Figure 63) were mostly neutral to alkaline. This could be a result of sampling of surface waters (except for one spring sample), but could also reflect streams draining weathering basalt flows, which contain abundant calcite amygdules. Interestingly, values were less acidic in October (7.18 in October vs. 6.80 in June and August) when water levels were lower. In June, there was a large percentage (~60%) of the 1st and 2nd order streams that were more acidic and this could be the result of more solutes entering the water due to accelerated weathering.

Total Dissolved Solids and Conductivity

Total dissolved solids (Figure 64 to Figure 66) and conductivity (Figure 67 to Figure 69) correlate reasonably well. Both variables show patterns of higher values in the eastern part of the study area. Patterns are very consistent regardless of seasons, even though values are about double in August and October than June.

Turbidity

Turbidity (Figure 70 to Figure 72) is a good indicator of the presence of suspended material in the water such as mineral particulates, colloids and organics. Results show that higher turbidity occurs mainly in 1st and 2nd order streams. Overall values in June are twice as high as the August results, while October shows a wider range that is likely due to the varied precipitation.

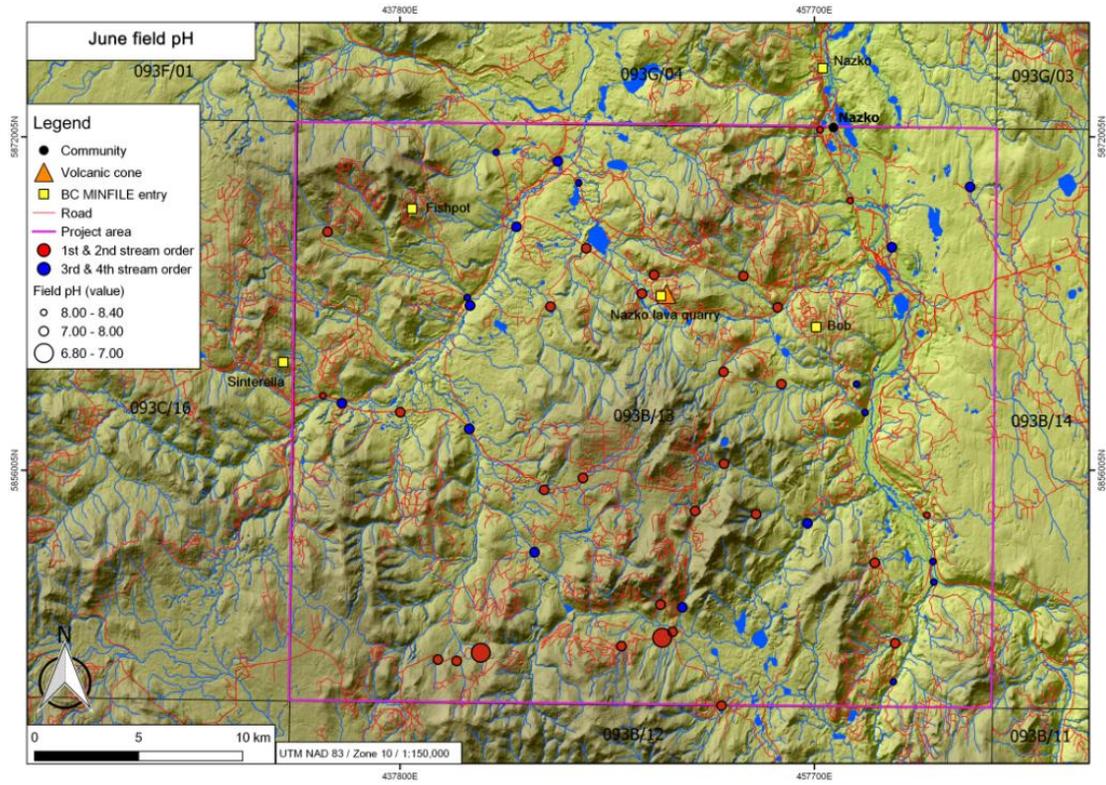


Figure 61. June pH results.

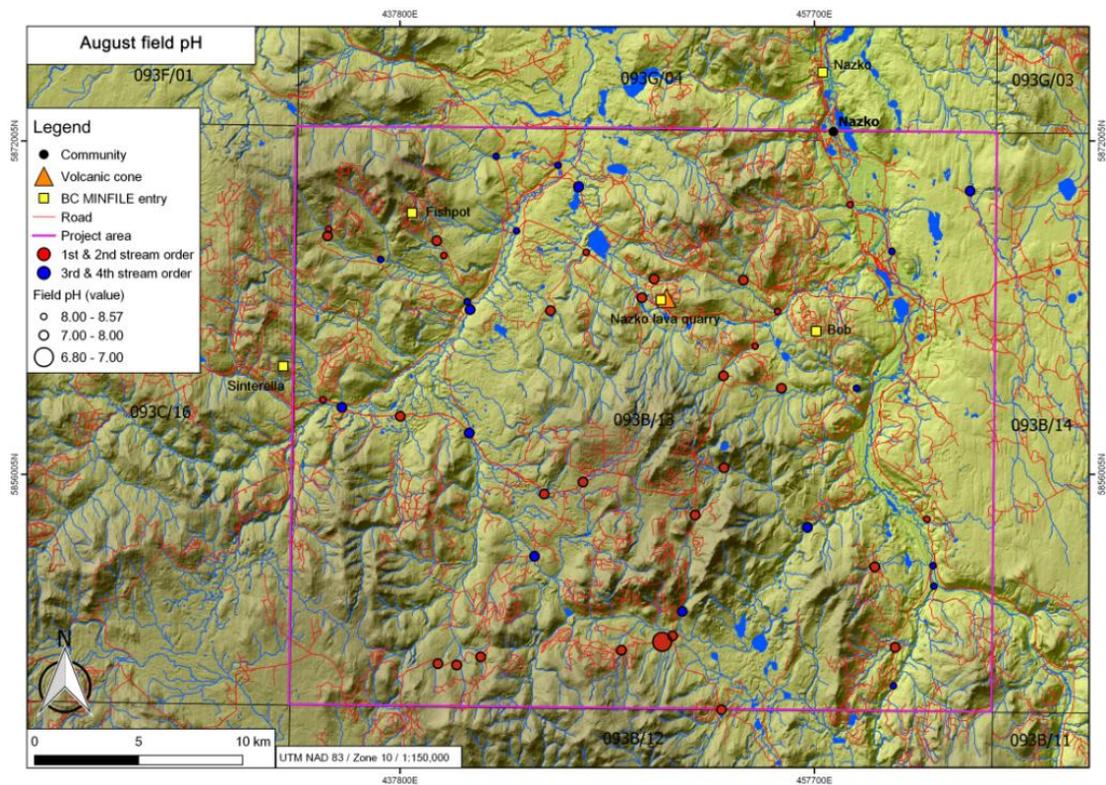


Figure 62. August pH results.

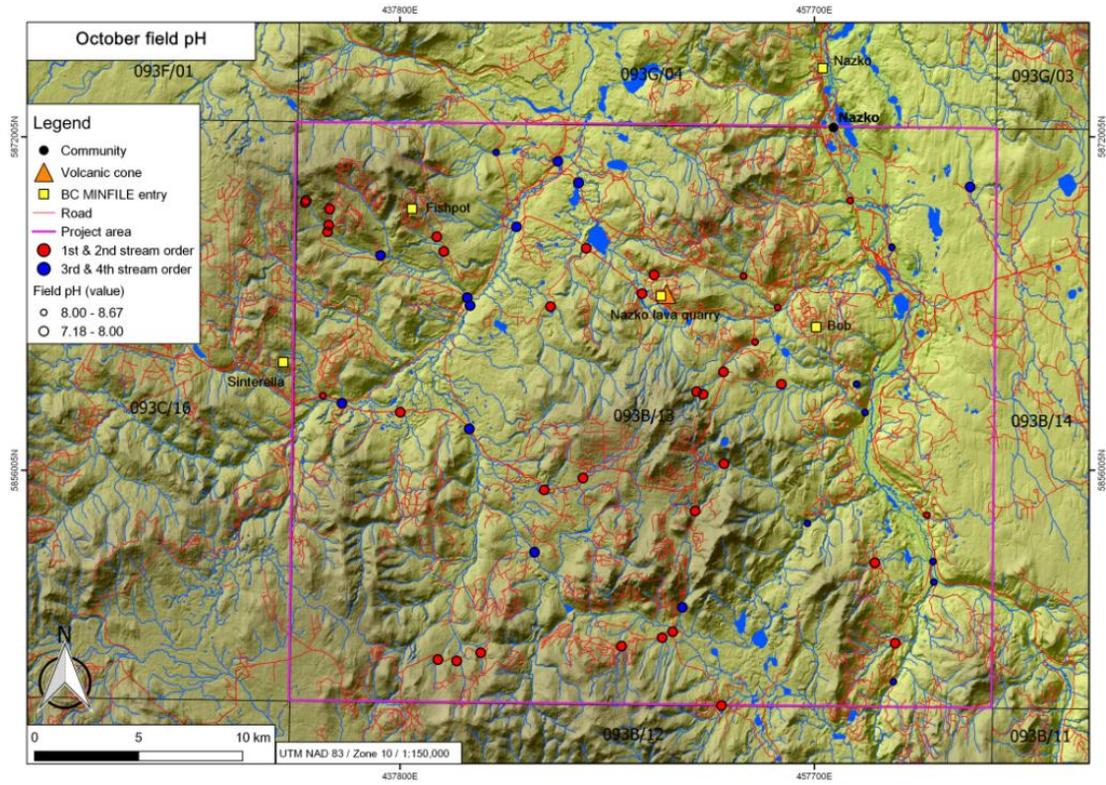


Figure 63. October pH results.

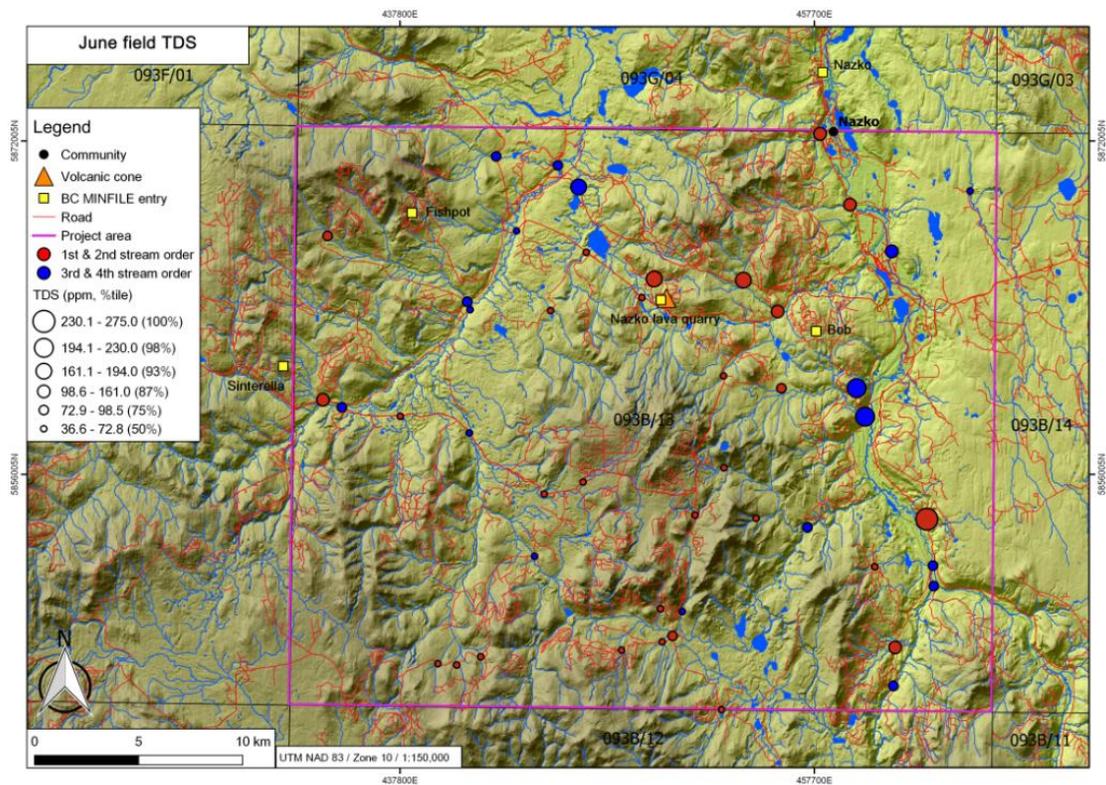


Figure 64. June TDS results.

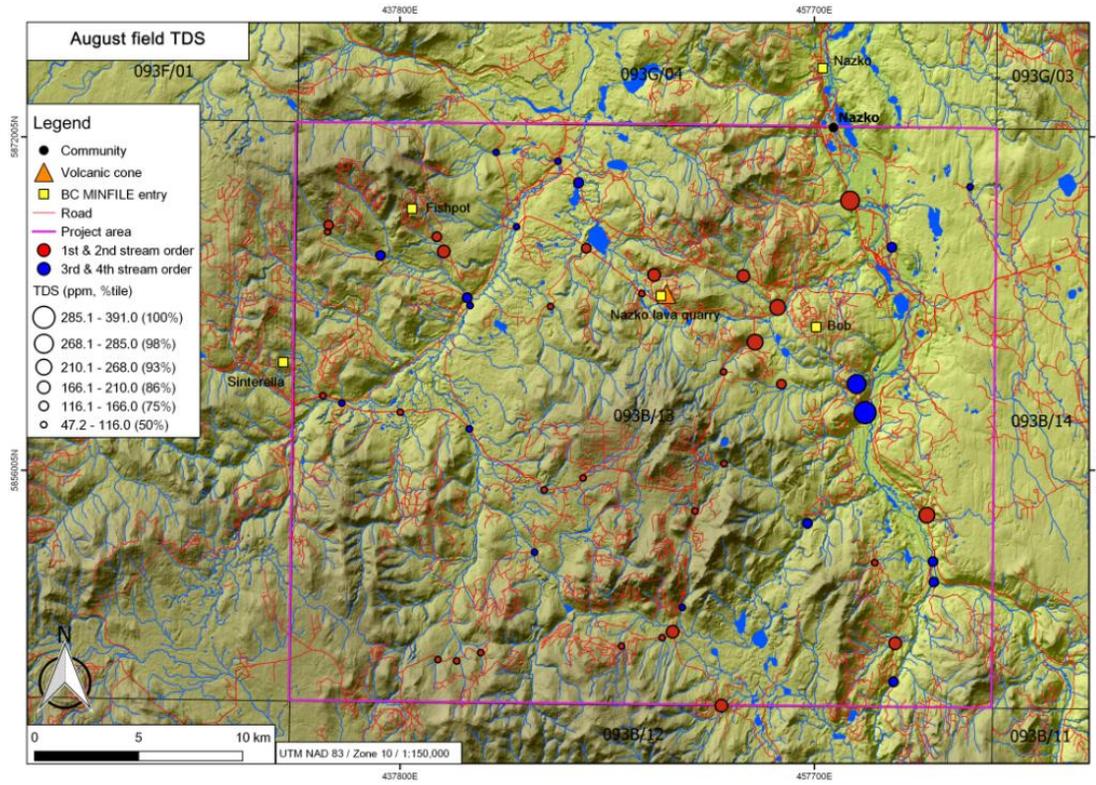


Figure 65. August TDS results.

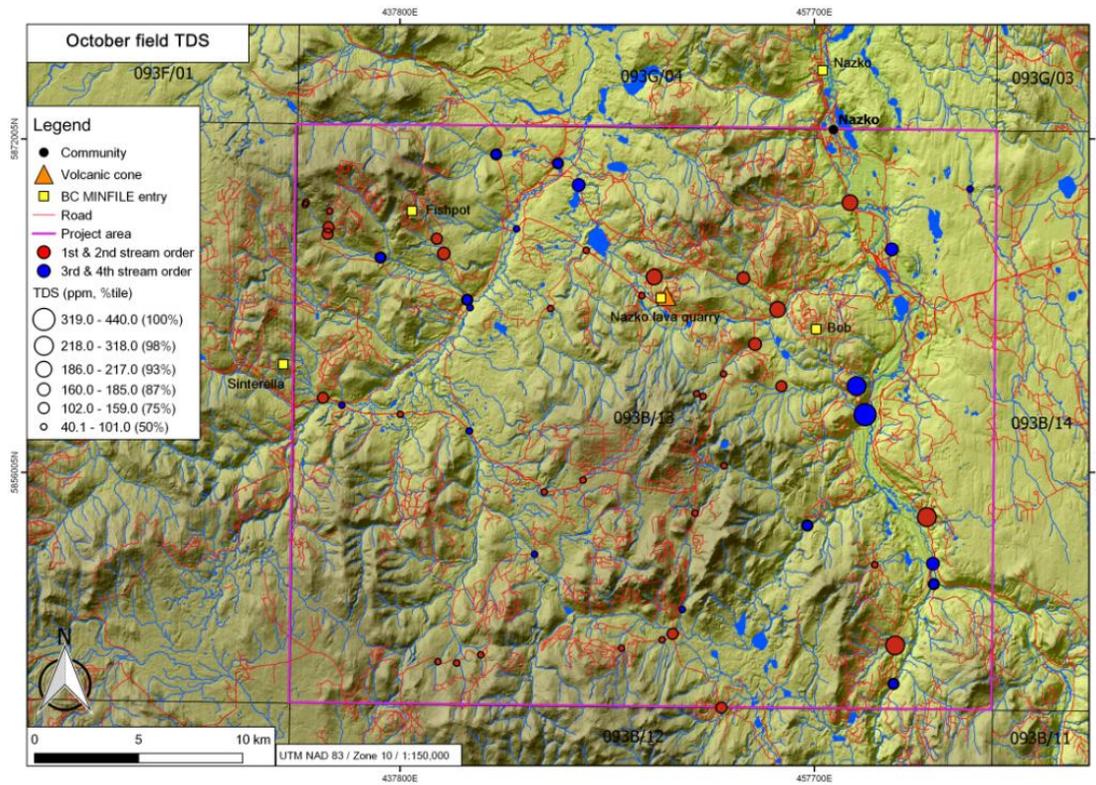


Figure 66. October TDS results.

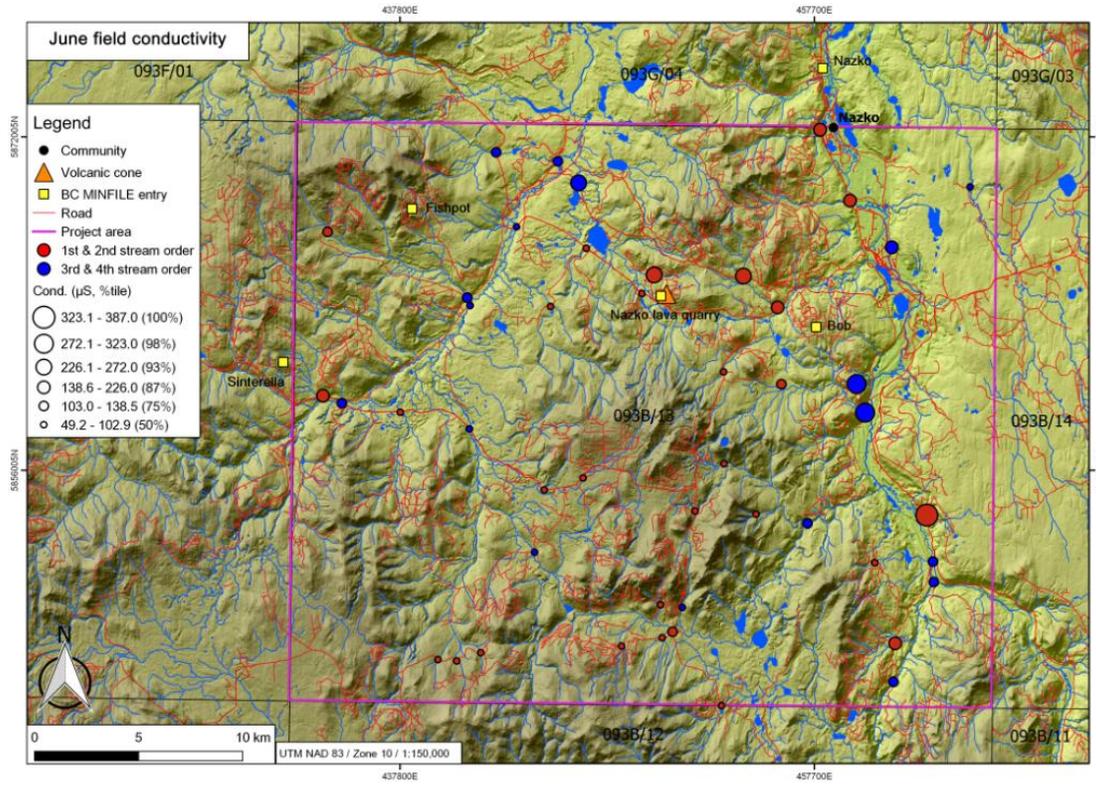


Figure 67. June conductivity results.

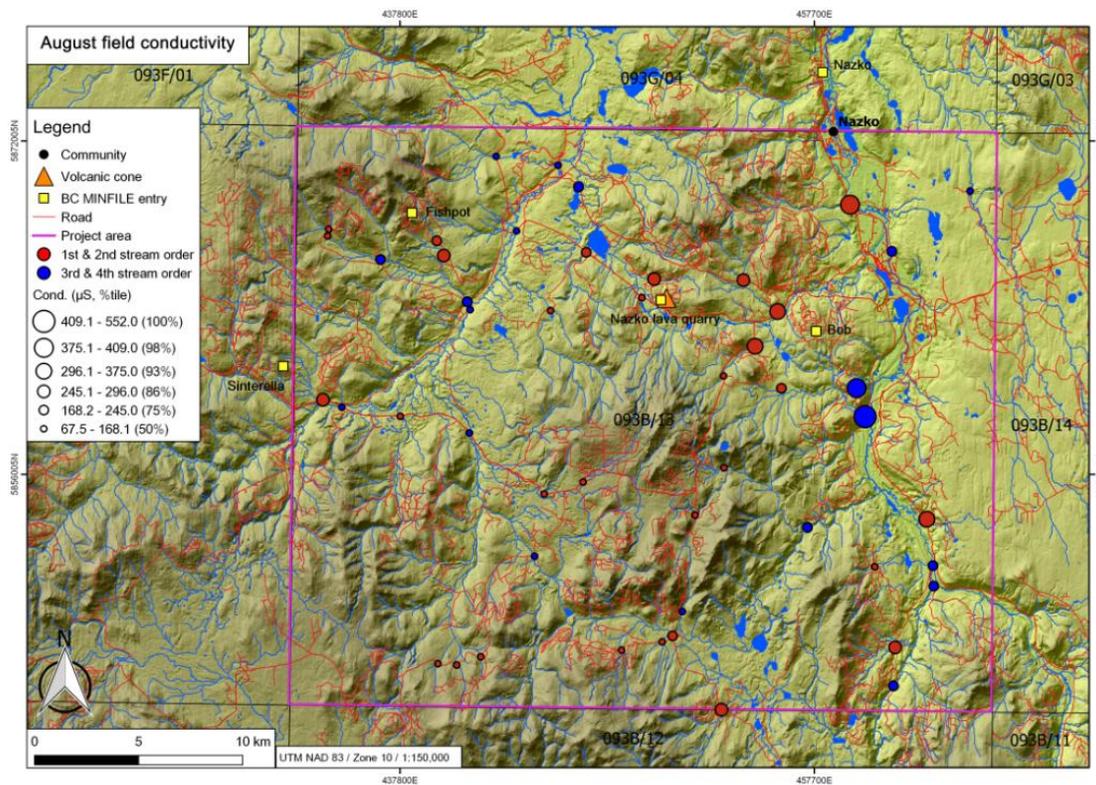


Figure 68. August Oakton PCS Testr 35 field conductivity.

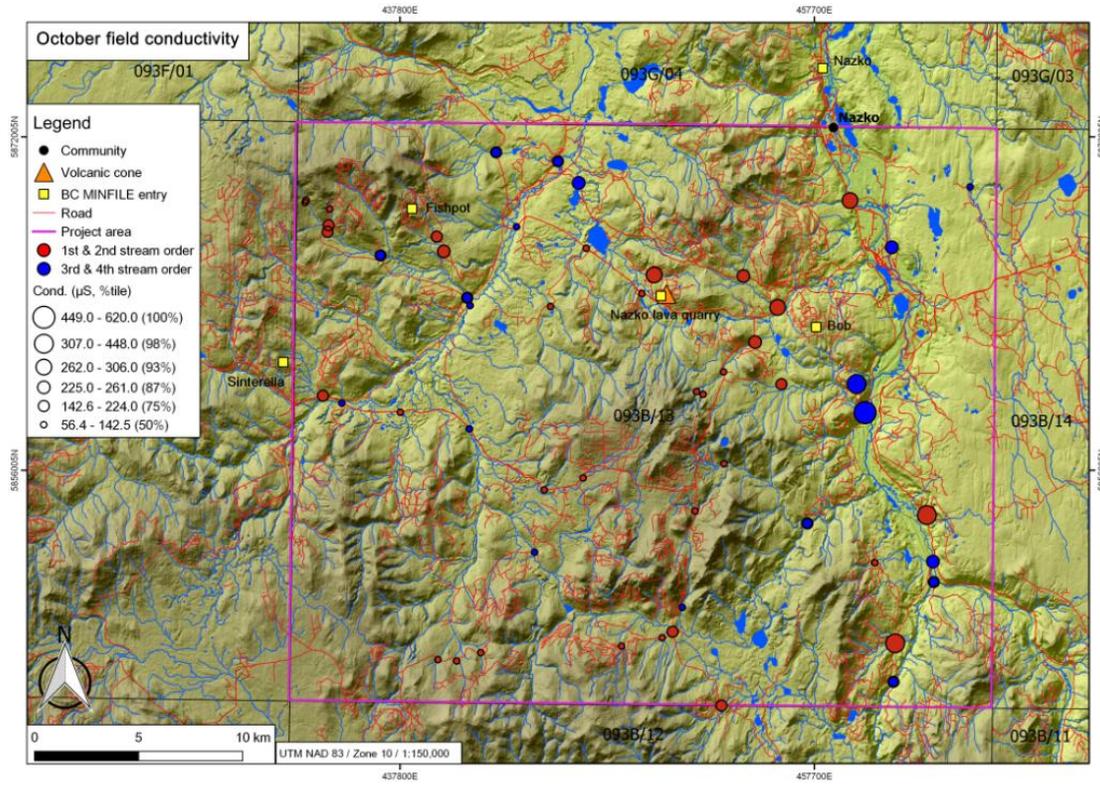


Figure 69. October conductivity results.

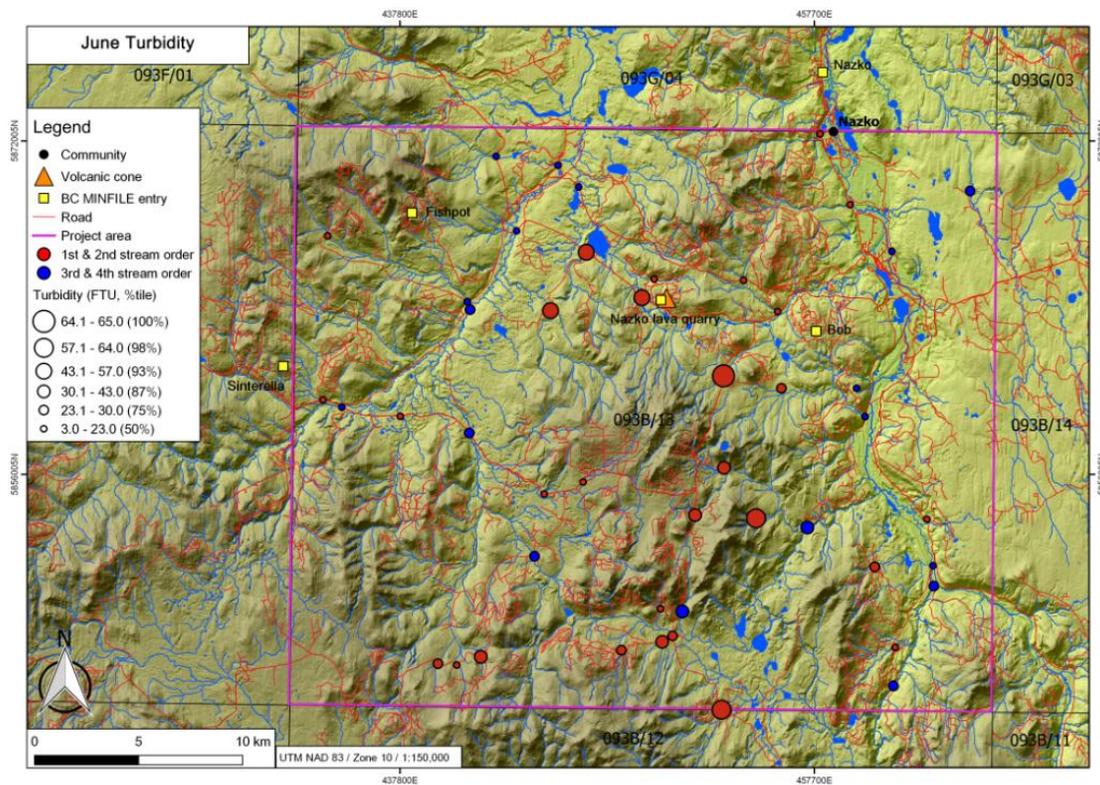


Figure 70. June photometer turbidity results.

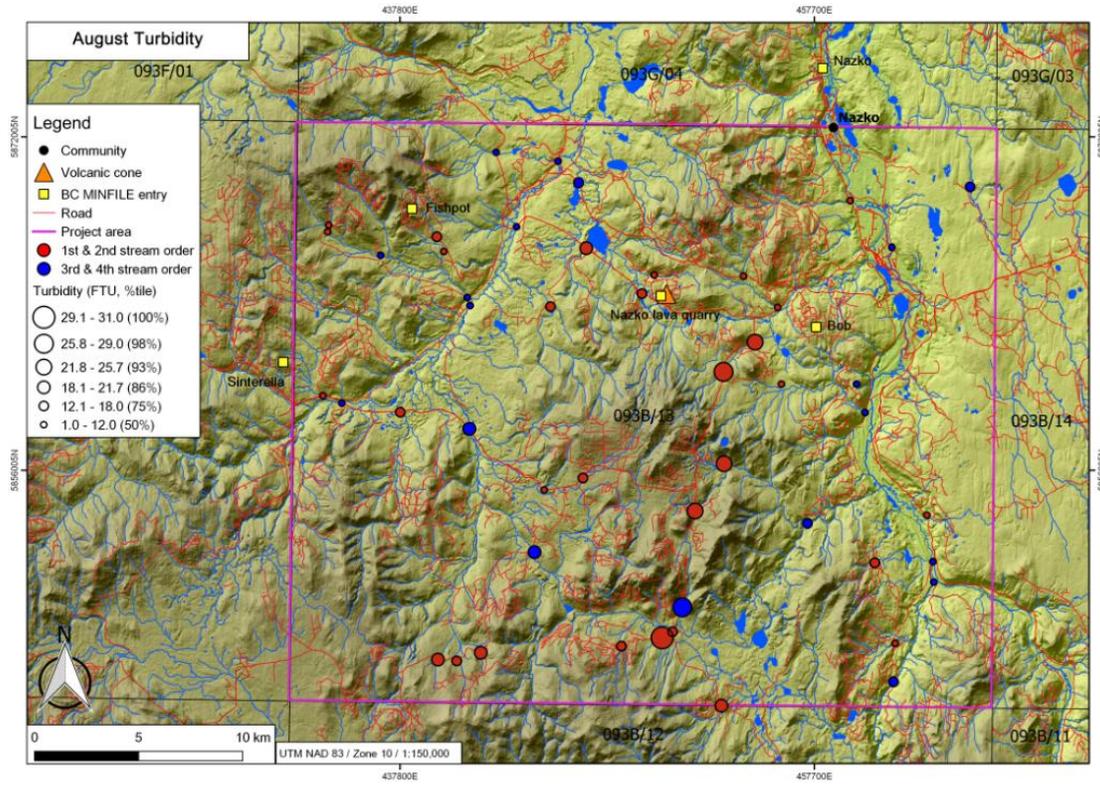


Figure 71. August photometer turbidity results.

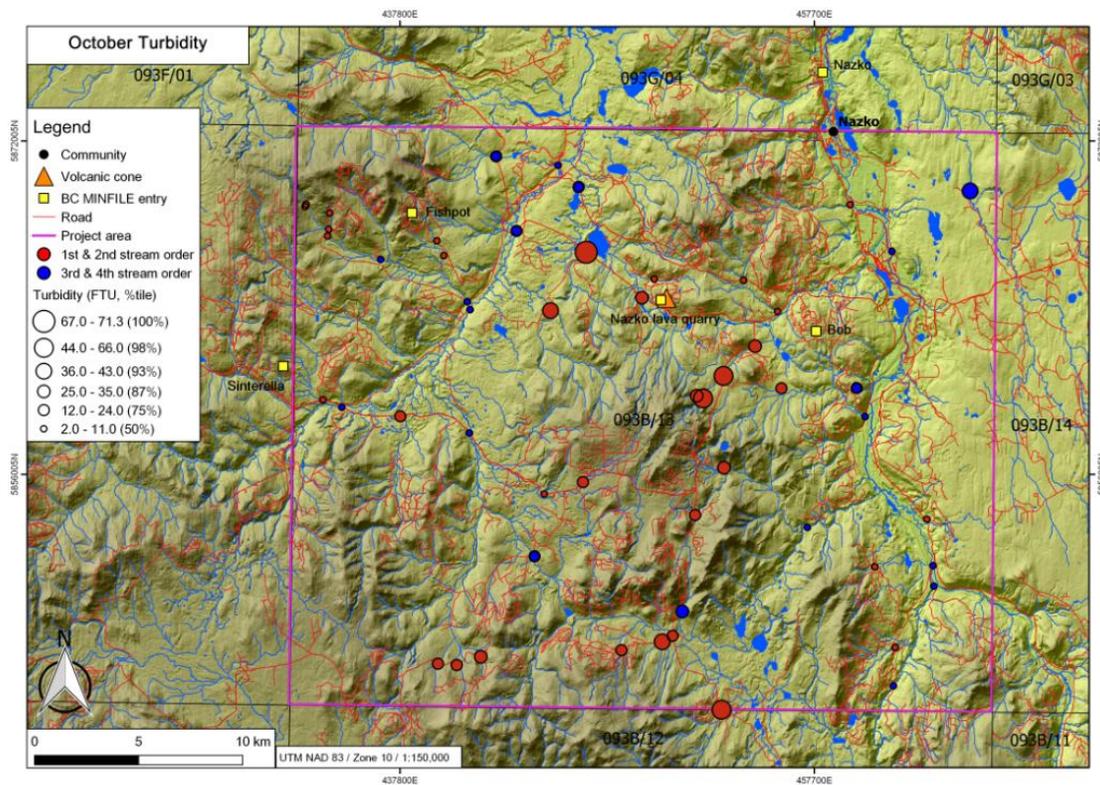


Figure 72. October photometer turbidity results.

Commodity Elements

Copper

Total Cu values in 1st and 2nd order streams (Figure 73 and Figure 74) are elevated southwest of both the Bob (about 4 km) and Fishpot (about 2 km). Note the three locations with elevated October values in the southeast corner of the study area (Figure 74). These locations correlate well with Al, Cl⁻ and SO₄ (see below).

Ionic Cu results (for photometer, Figure 75 and Figure 76; PDV – Figure 77) show a good correlation for August and October at the Bob showing, and in October for Fishpot for the PDV. The August results confirm the Cu (total) results from near the Bob showing.

Iron

Iron displays comparable patterns for all three seasons (Figure 78 to Figure 80). This is regardless of maximum concentrations that are twice as high in August. Elevated concentrations do not seem to correlate to known mineral showings and are not exclusive to 1st and 2nd order streams.

Molybdate

Molybdate (Figure 81 and Figure 82) shows a positive response near the Bob and Fishpot occurrences. August results correlate with the elevated Cu value detected south west of Bob, and in October with many of the positive soluble Cu responses. There is an additional anomaly near to the southern project boundary. Elevated MoO₄ samples occur exclusively in 1st and 2nd order drainages. The median October concentration is twice as high as the August maximum concentration (0.30 mg/l vs. 0.17 mg/l).

Zinc

For Zn (Figure 83 to Figure 86), except for the EDTA correction for Cu interference, results are treated as Zn+Cu (as discussed earlier). Elevated concentrations occur only in 1st and 2nd order streams, especially in the June results. Values correlate well between the seasons, especially in lower order drainages. For the Zn EDTA test results, the elevated value at the southern area border correlates with the elevated MoO₄ and ionic Cu results discussed above. The 3rd order stream Zn EDTA value northwest of Nazko Cone (Figure 85) correlates with the Fe results.

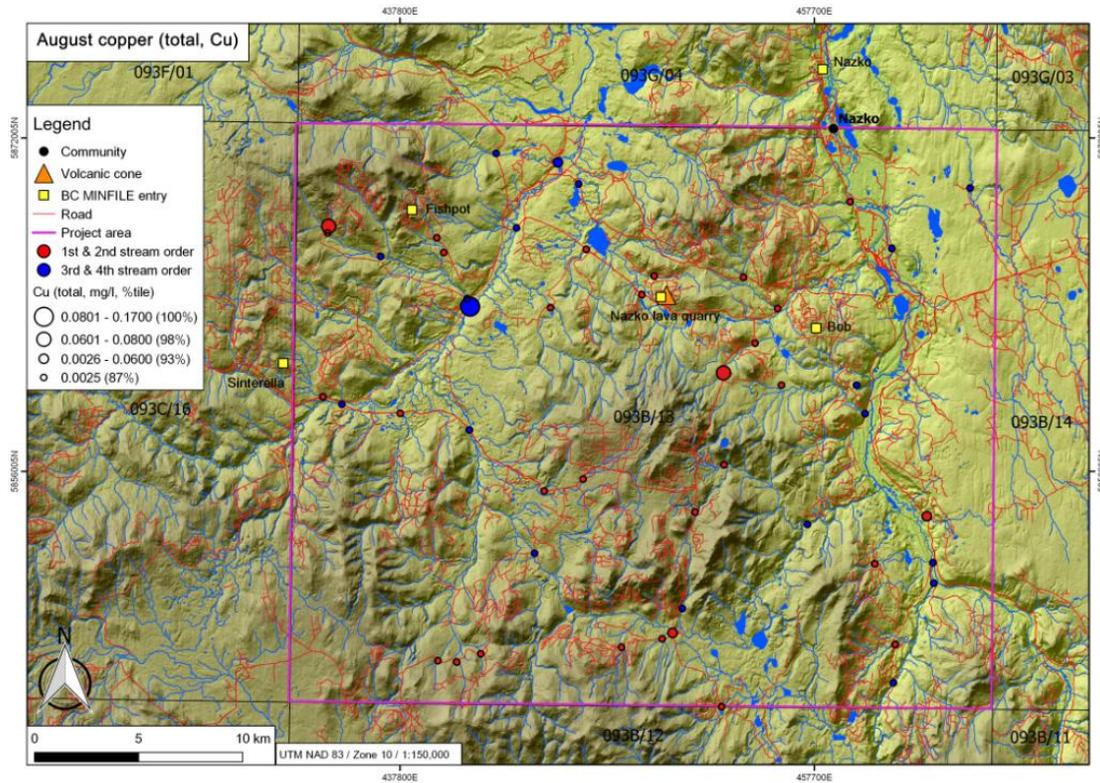


Figure 73. August photometer Cu (total) results.

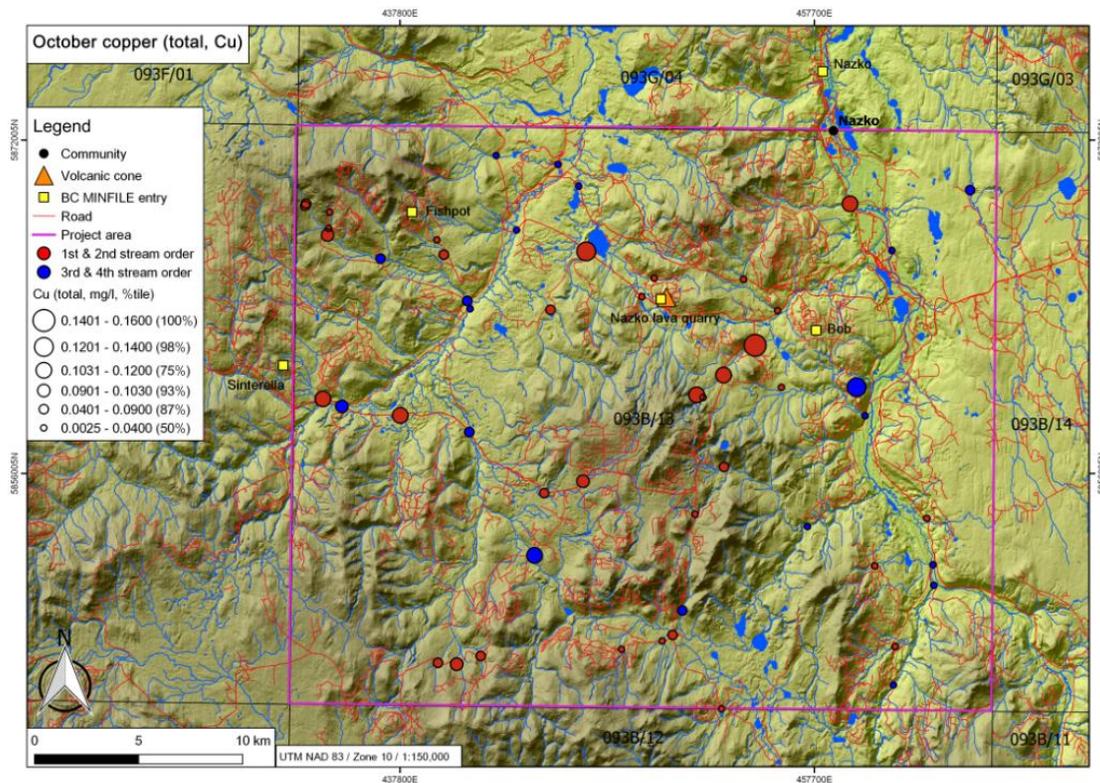


Figure 74. October photometer Cu (total) results.

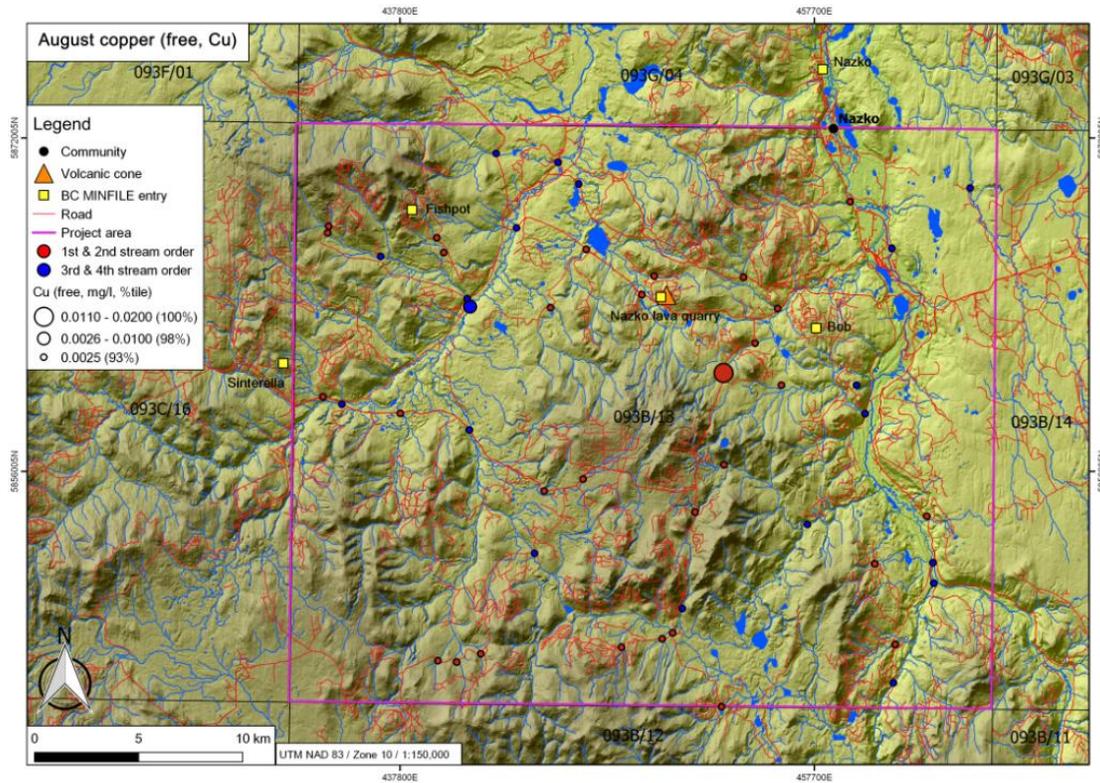


Figure 75. August photometer Cu (free) results.

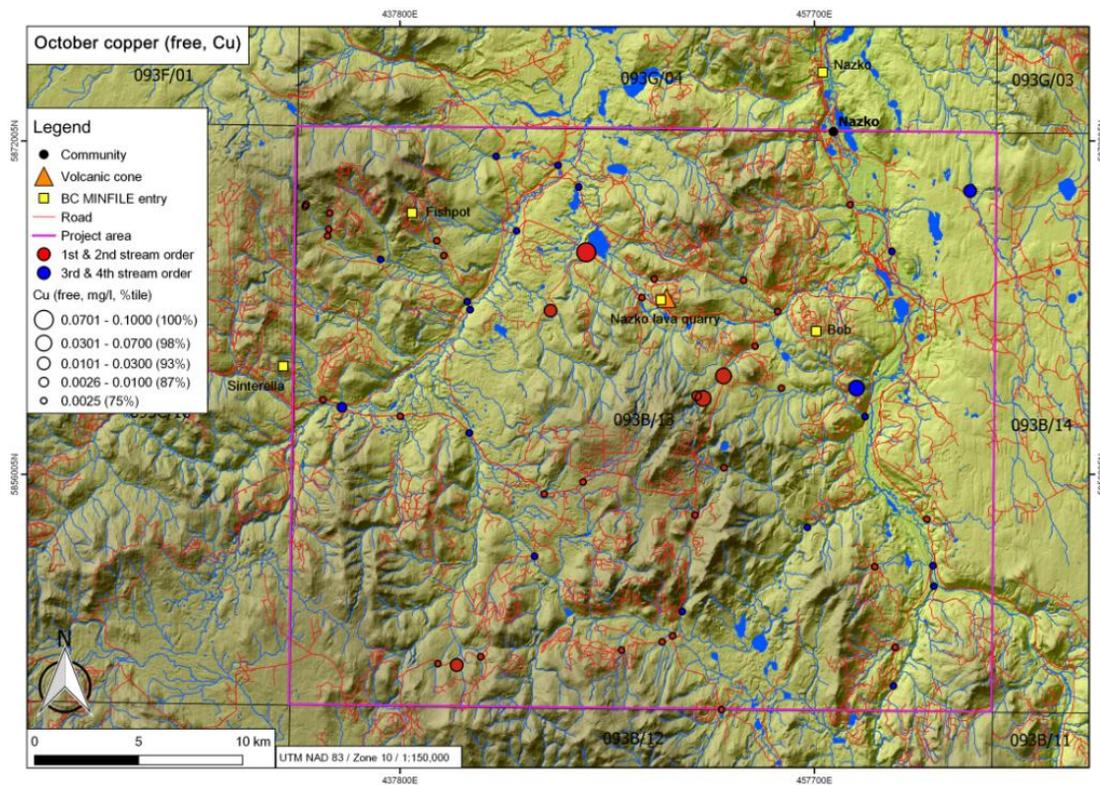


Figure 76. October photometer Cu (free) results.

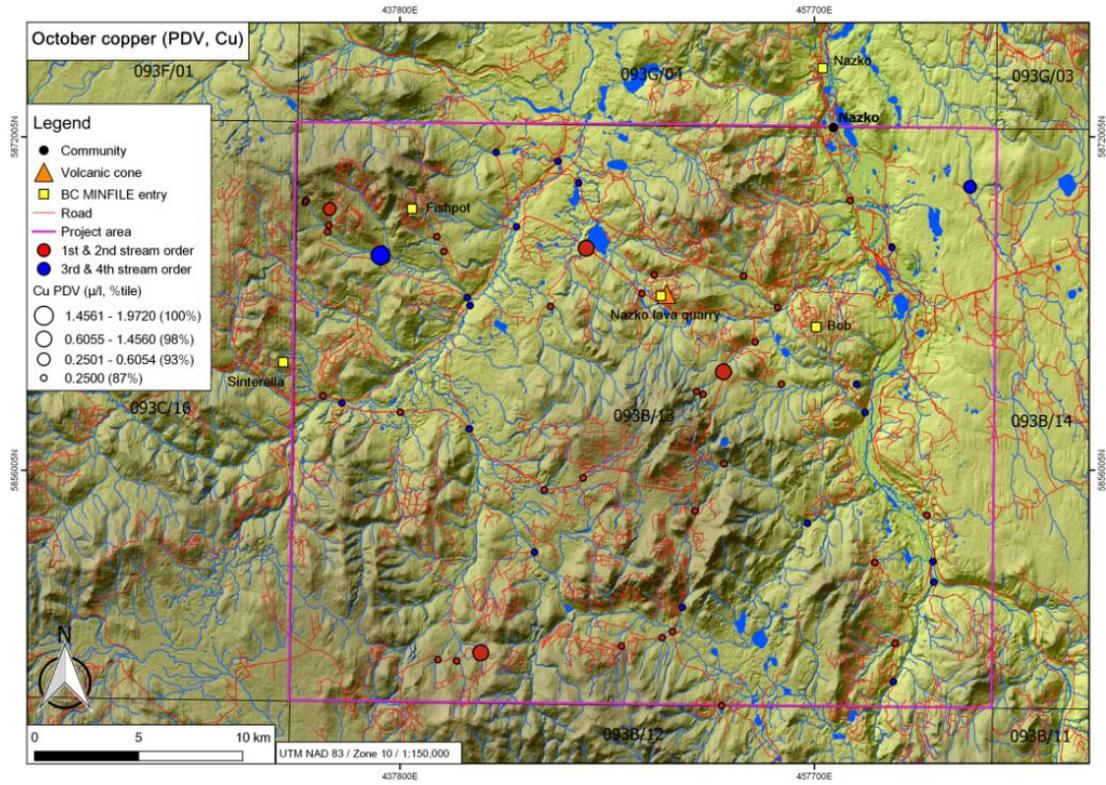


Figure 77. October PDV Cu (dissolved) results. Note units are in microgram/litre.

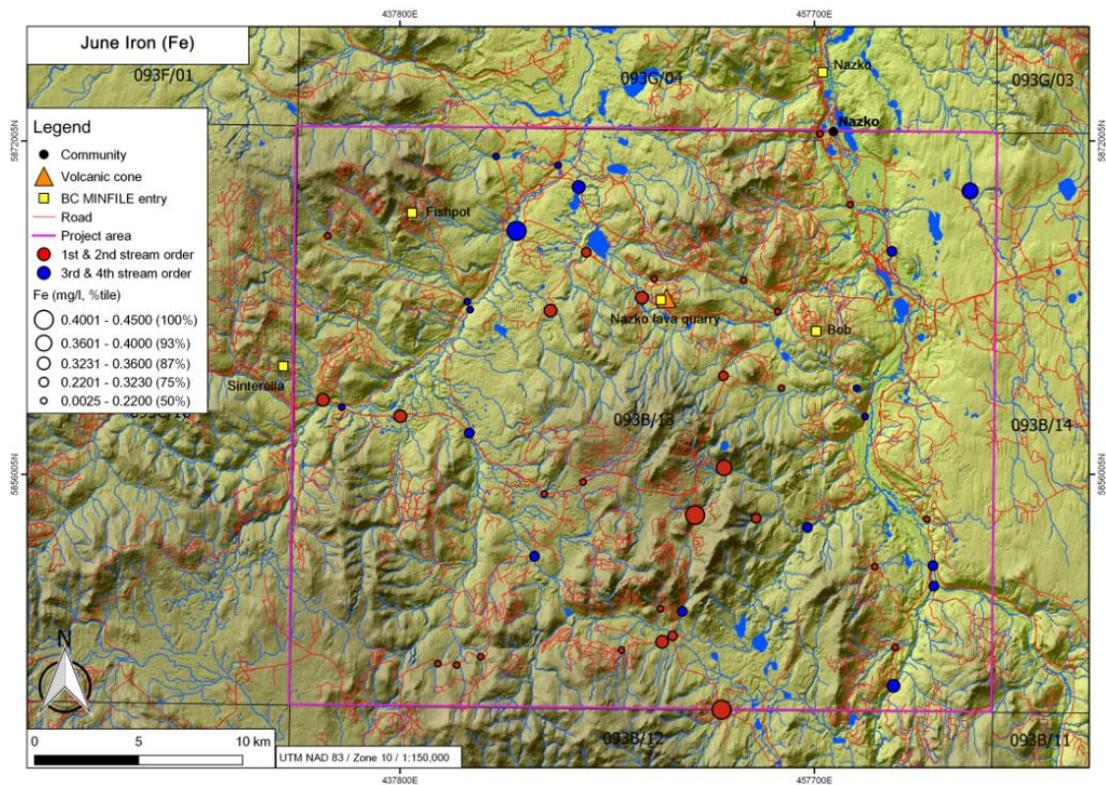


Figure 78. June photometer Fe results.

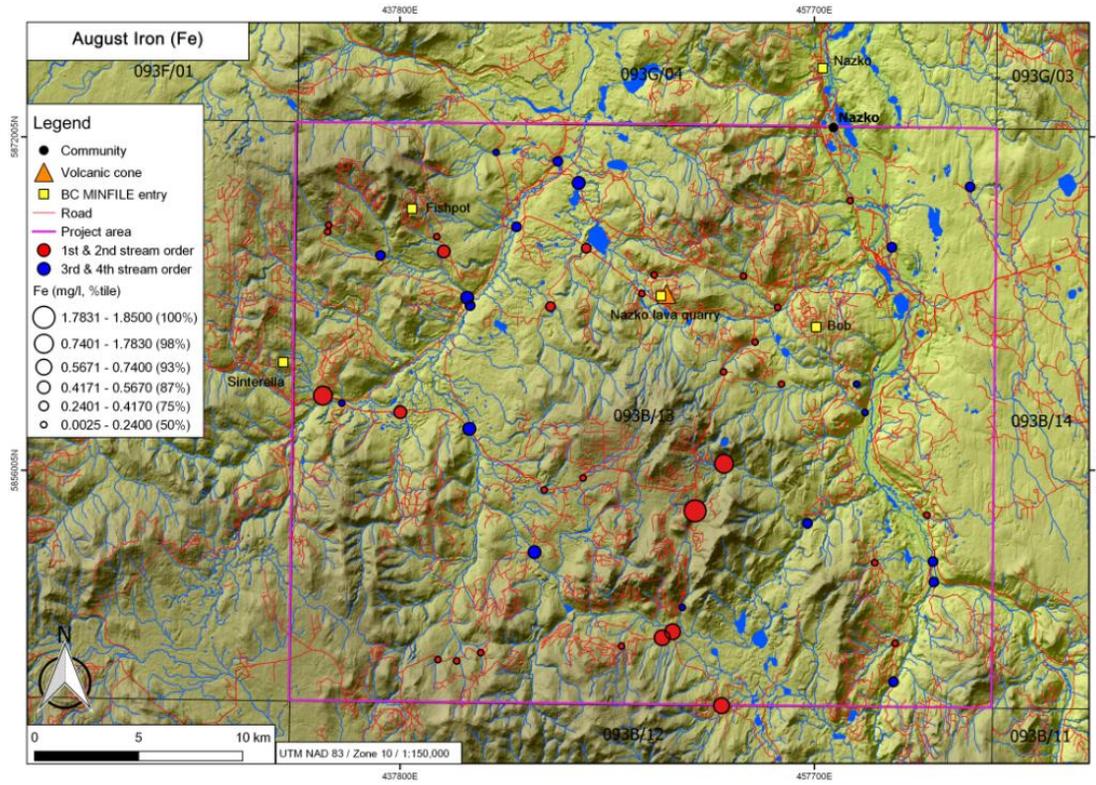


Figure 79. August photometer Fe results.

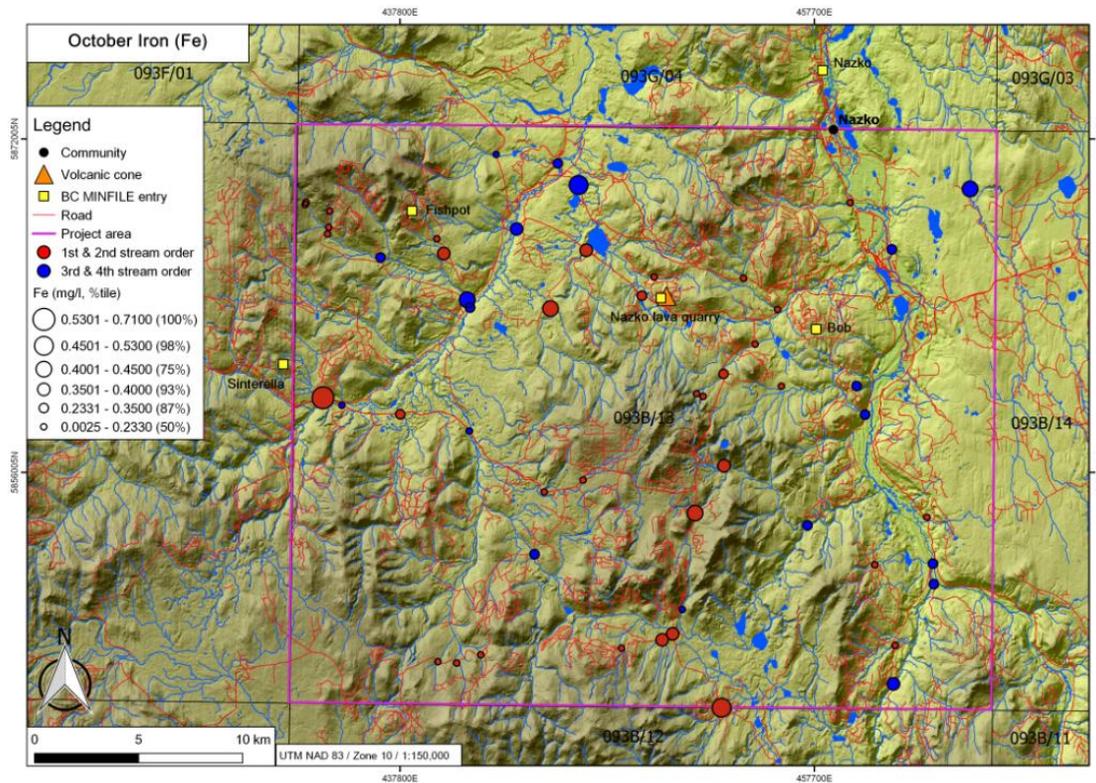


Figure 80. October photometer Fe results.

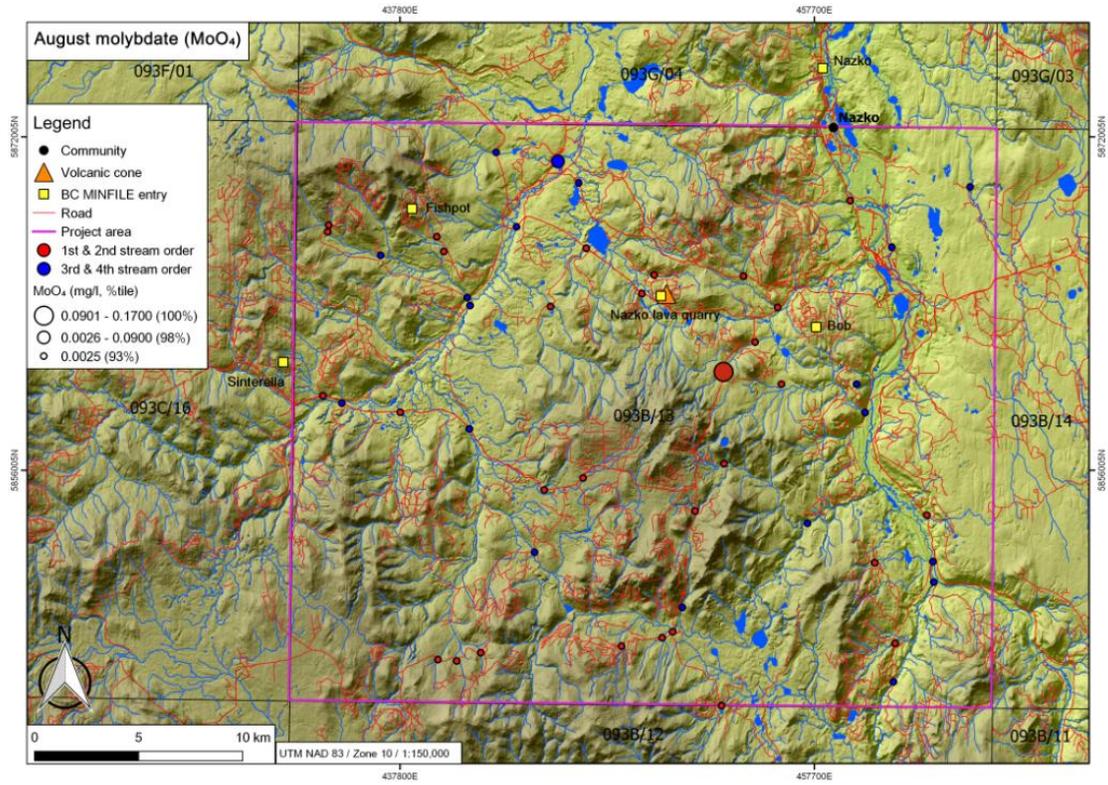


Figure 81. August photometer MoO₄ results.

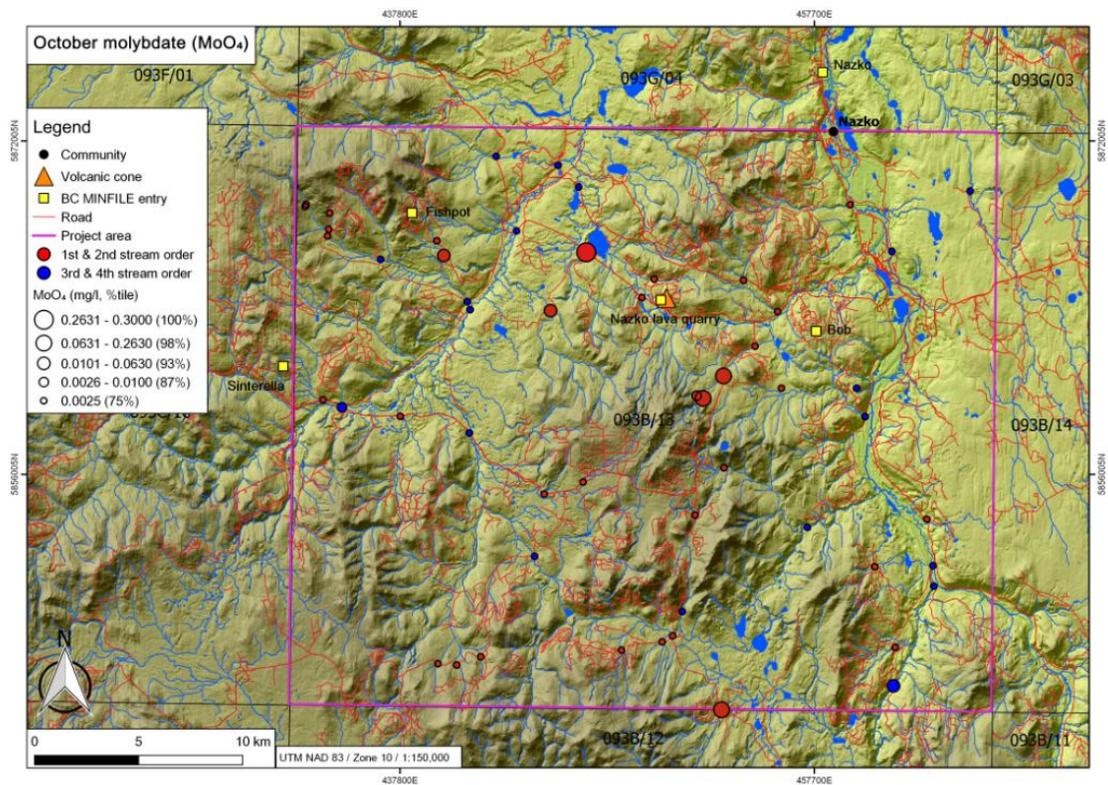


Figure 82. October photometer MoO₄ results.

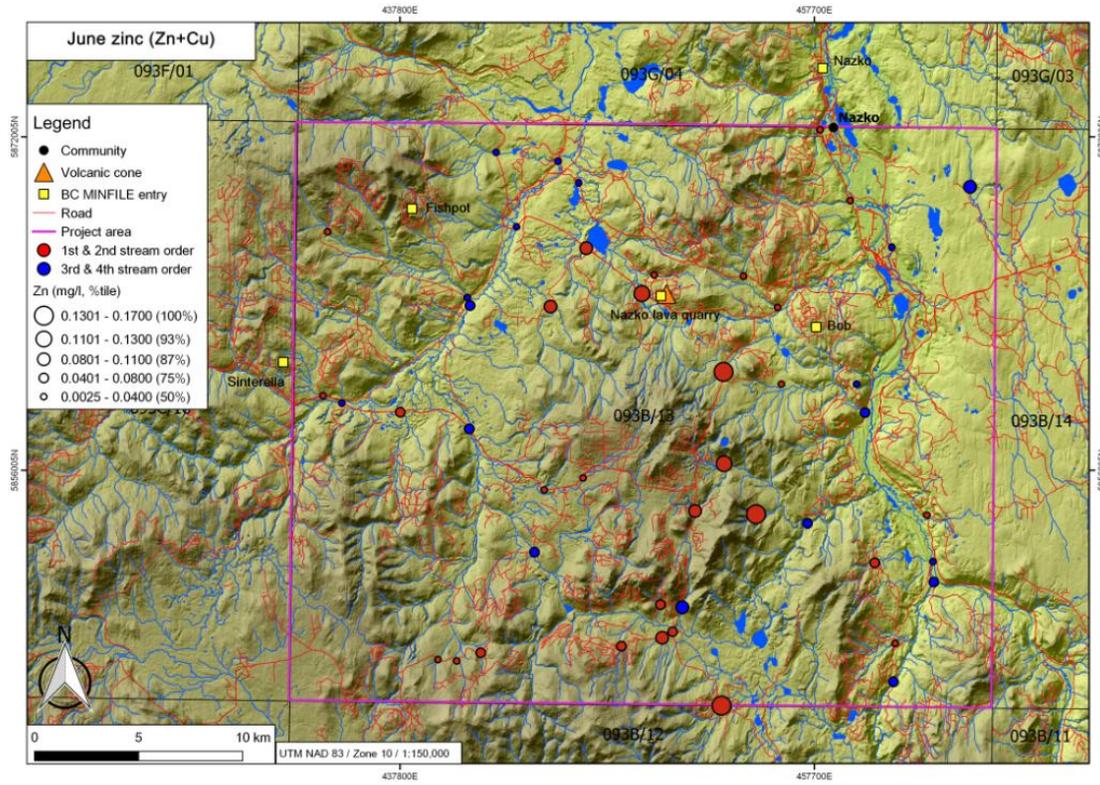


Figure 83. June photometer Zn+Cu results.

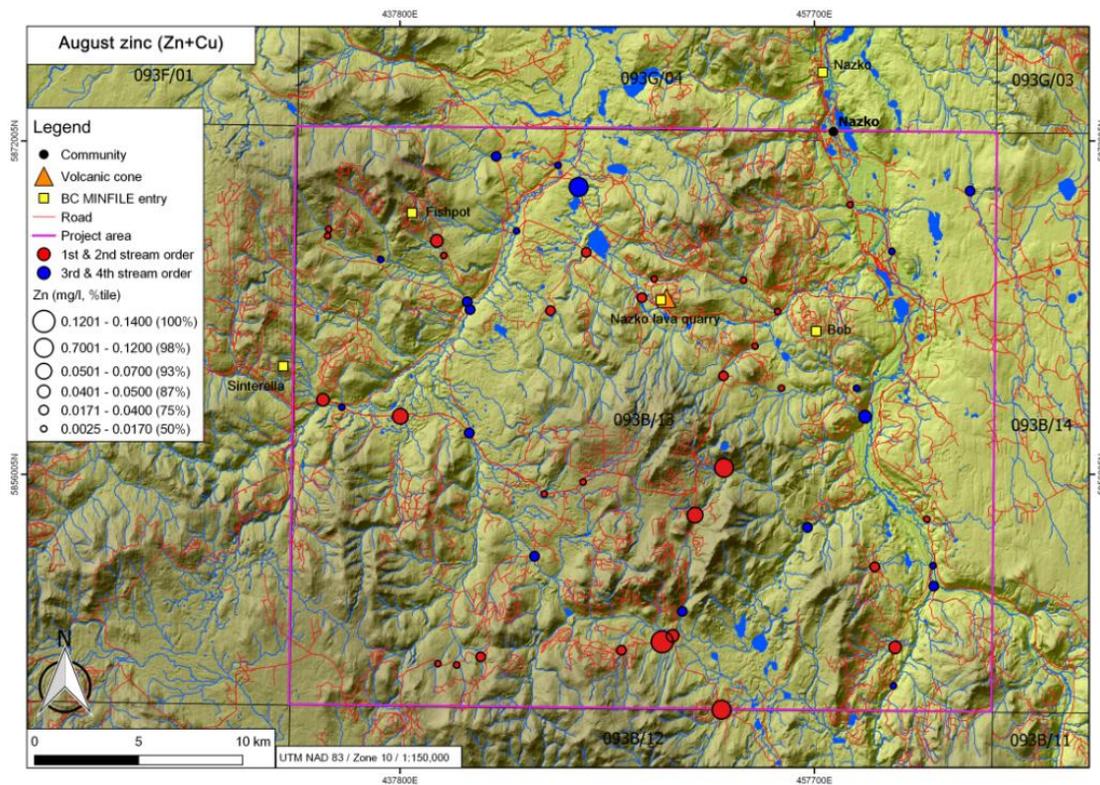


Figure 84. August photometer Zn+Cu results.

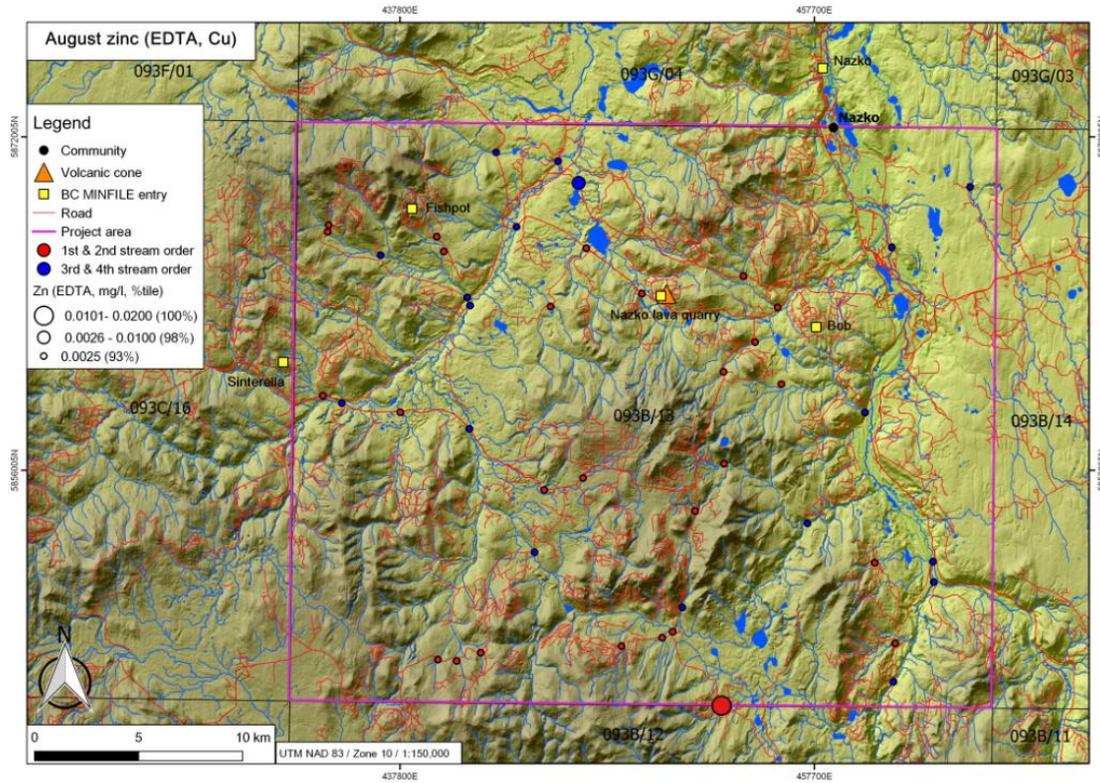


Figure 85. August photometer Zn EDTA results.

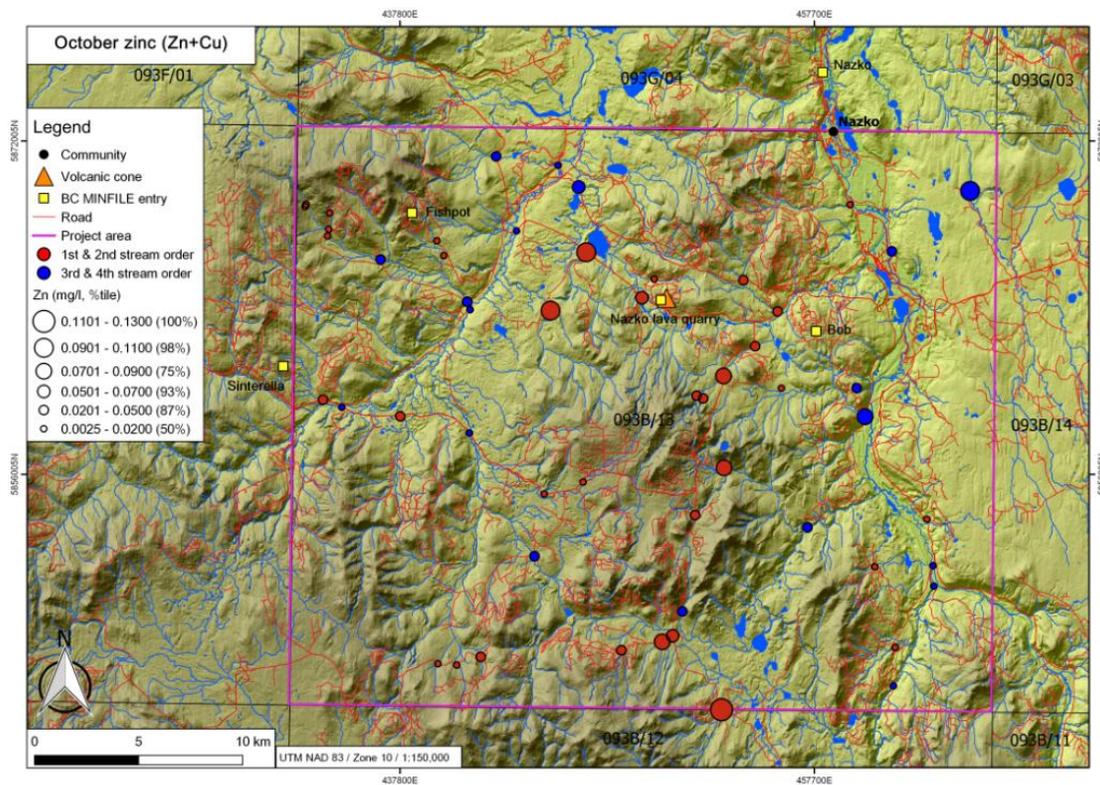


Figure 86. October photometer Zn+Cu results.

Other Elements and Anions

Chloride

Elevated Cl^- values occur mostly in 1st and 2nd order drainages (Figure 87 to Figure 89). The results may be influenced by higher water turbidity, by the clearer solution at lower concentrations, or simply having increased values due to accelerated weathering during precipitation events. Results show consistent elevated value at the sample site to the southeast of the Bob showing, which is also associated with elevated Cu and MoO_4 values. Elevated Cl^- values also correlate with Al and SO_4 results with the three points in the south-east corner of the study area.

Fluoride

Fluoride values (Figure 90 to Figure 92) show a steady concentration range between the seasons (1.148 mg/l to 1.407 mg/l), but do not display consistent patterns. Fluoride correlates strongly with other commodity analytes (Cu and MoO_4) in the October results southwest of Bob.

Arsenic

Elevated As concentrations (Figure 93 and Figure 94) occur to the south of Fishpot. Both the August and October results correlate well. Concentrations decrease along the drainage from the northeast to southwest over a distance of about 10 km, with values ranging from about 10 μl to about 3 μl . The catchment basin extends for an additional 3-4 km to the northwest beyond the highest elevation sample. Interestingly, two of the locations with elevated As concentrations are from 3rd and 4th stream order streams, with two additional stations downstream from the 1st and 2nd order.

Aluminum

Aluminum concentrations (Figure 95 to Figure 97) are inconsistent at each location, but higher concentrations show a preference for 1st and 2nd order streams. Concentrations in June and October are higher than August; another indication of the effect of increased weathering during increased precipitation events. Results correlate strongly across the seasons at the locations southwest of the Bob showing and at the three points in the southeast of the study area.

Calcicol and Hardicol

Calcicol (calcium hardness; Figure 98 to Figure 100) and Hardicol results (total hardness; Figure 101 to Figure 103) both correlate well. The tests display stable results over all three seasons. Results are strongly correlated to K and Mg.

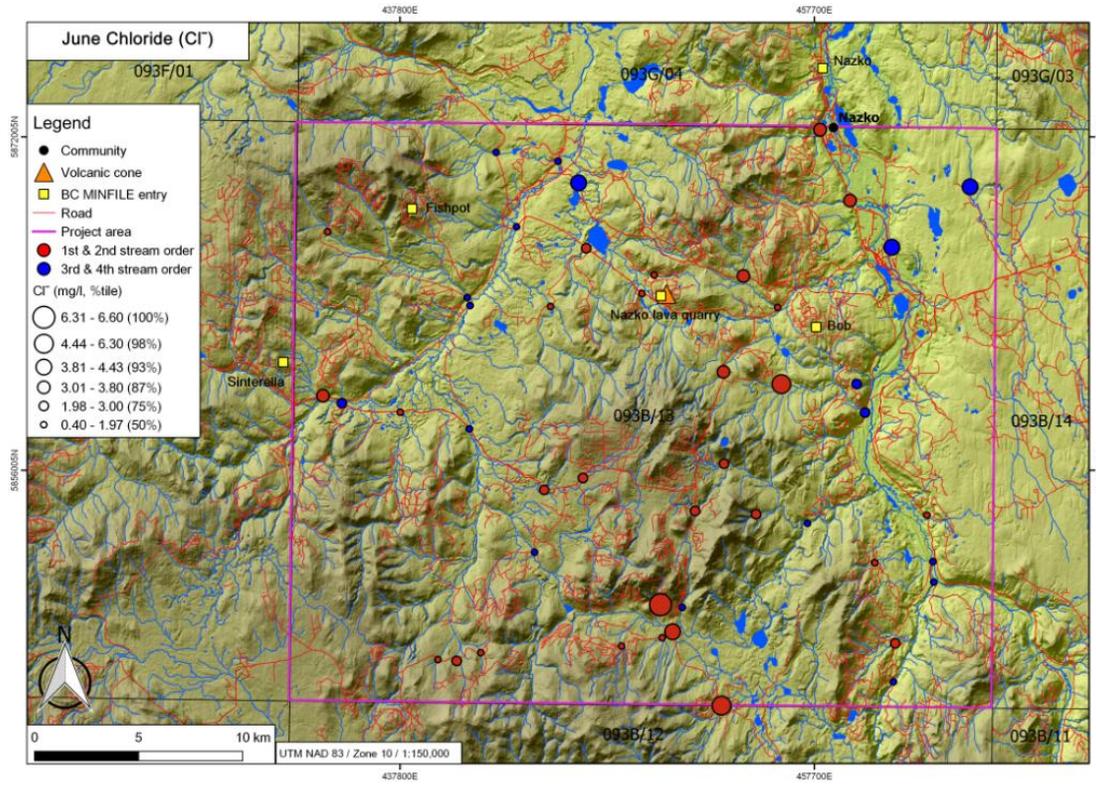


Figure 87. June photometer Cl⁻ results.

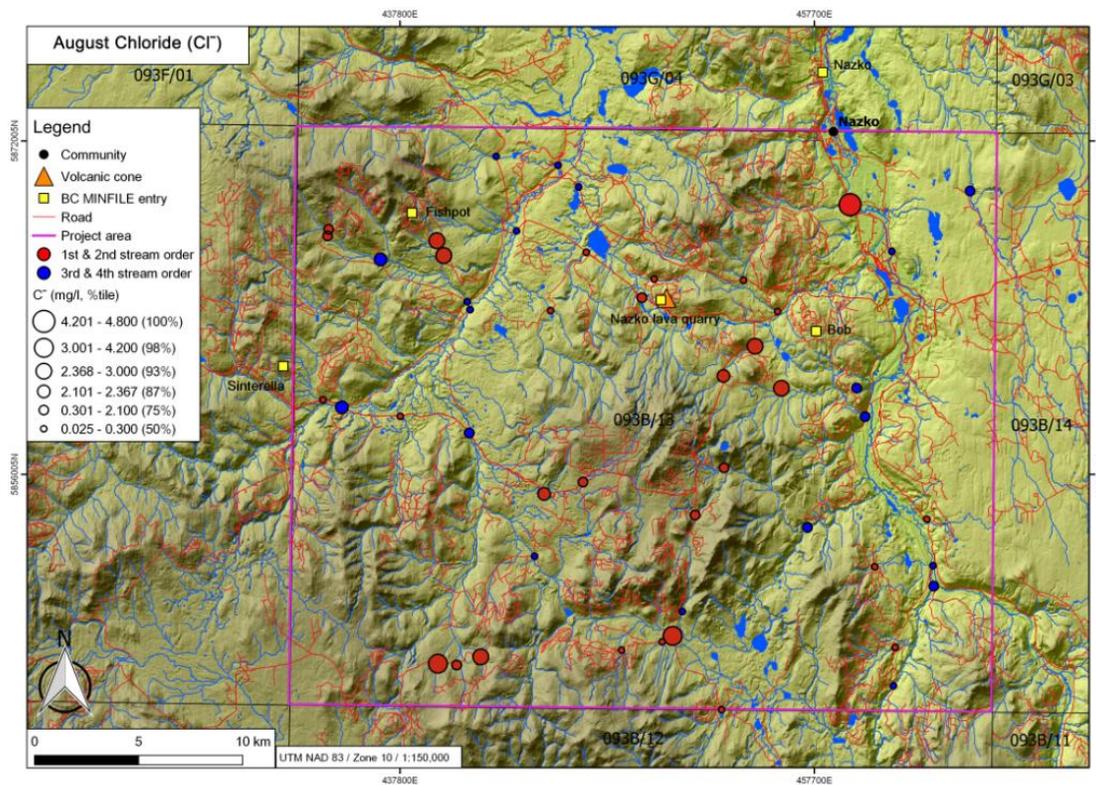


Figure 88. August photometer Cl⁻ results.

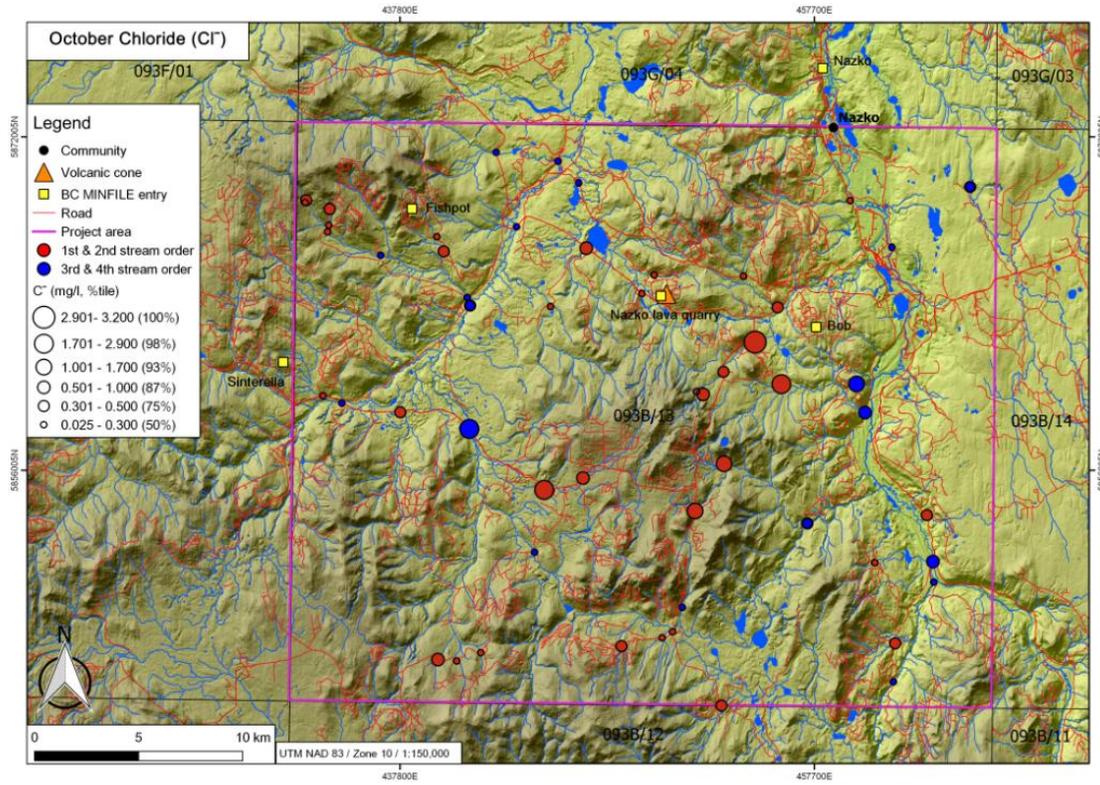


Figure 89. October photometer Cl⁻ results.

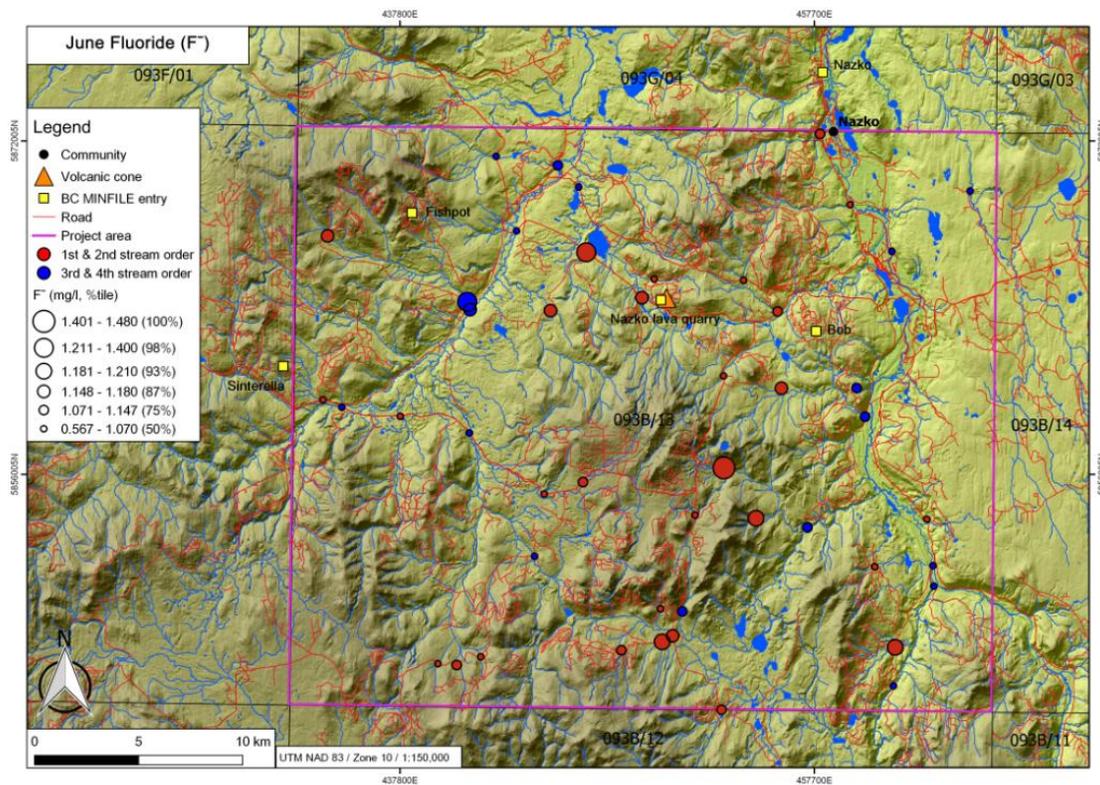


Figure 90. June photometer F⁻ results.

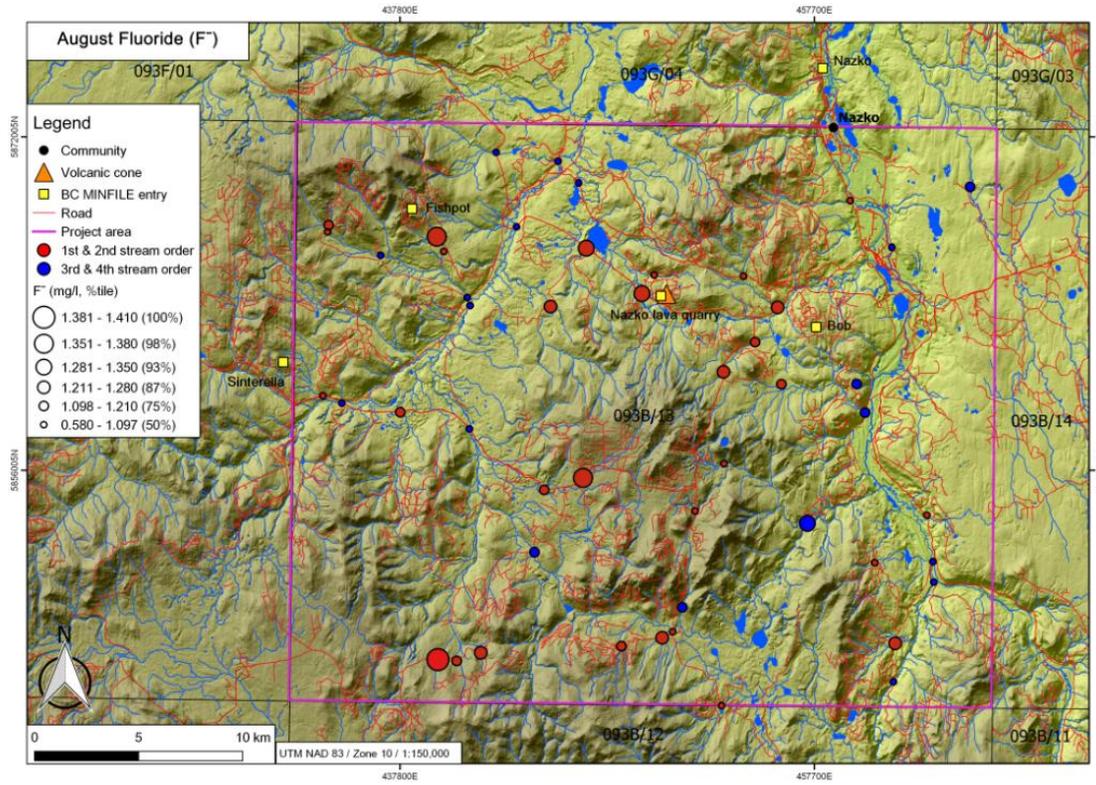


Figure 91. August photometer F⁻ results.

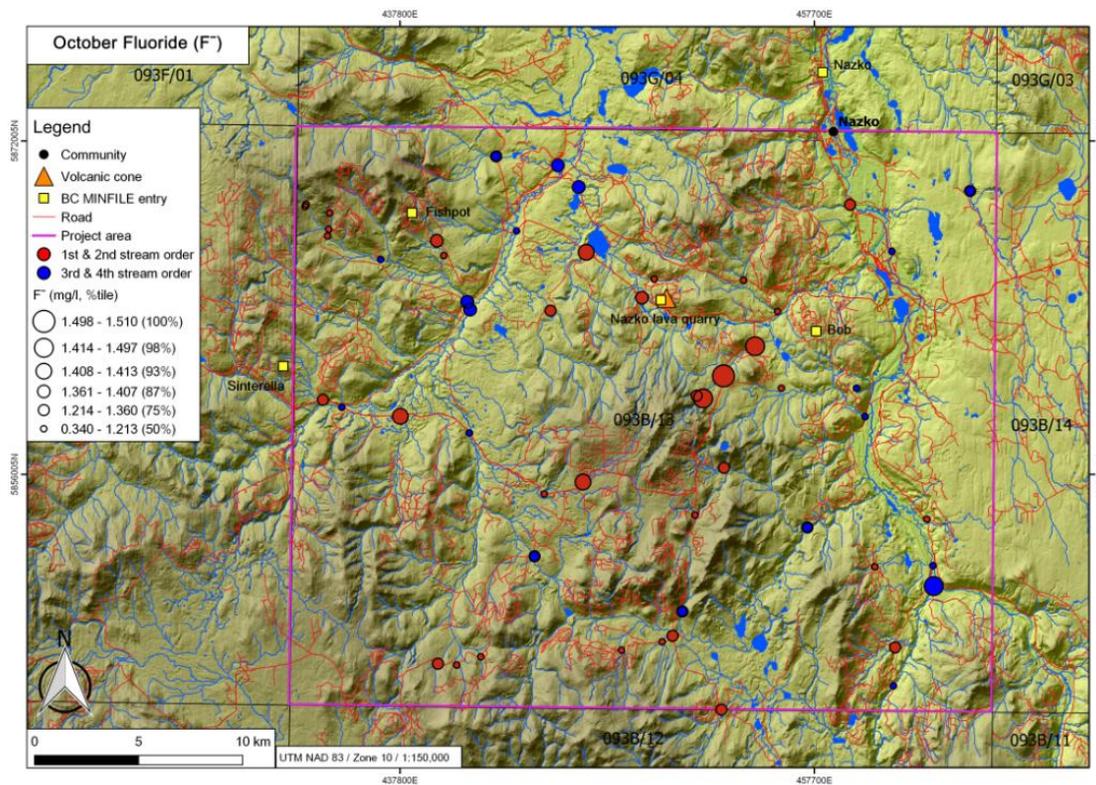


Figure 92. October photometer F⁻ results.

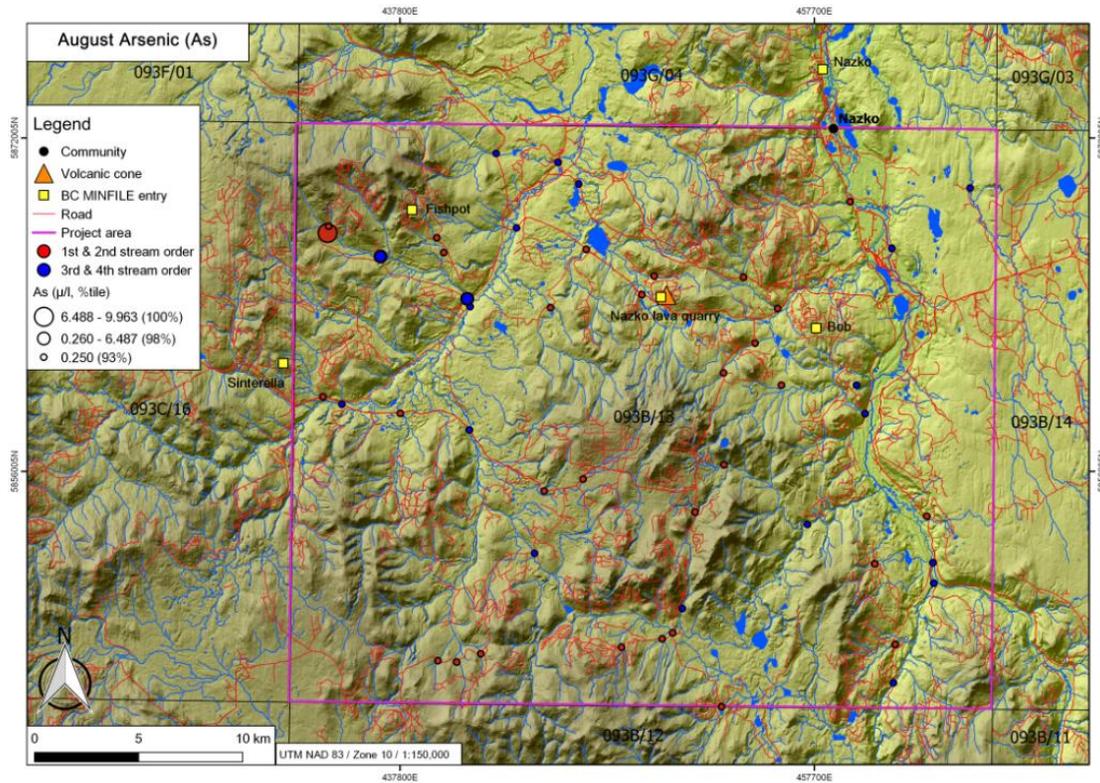


Figure 93. August PDV As results. Note units are in microgram/litre.

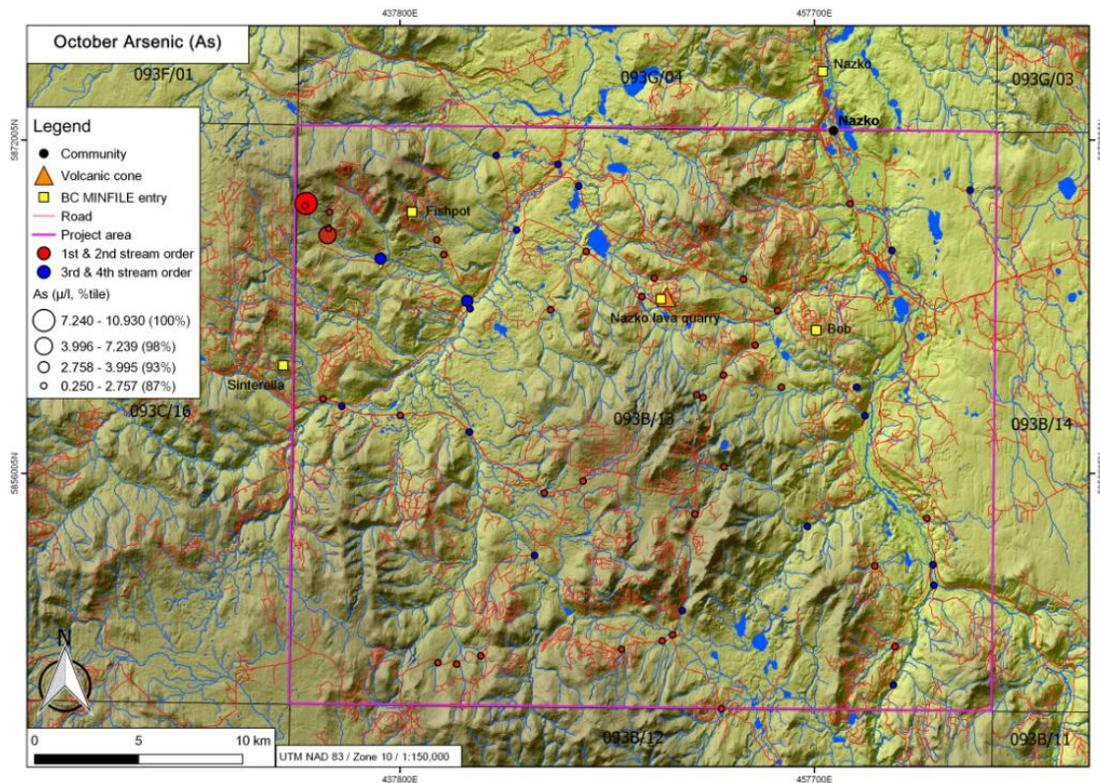


Figure 94. October PDV As results. Note units are in microgram/litre.

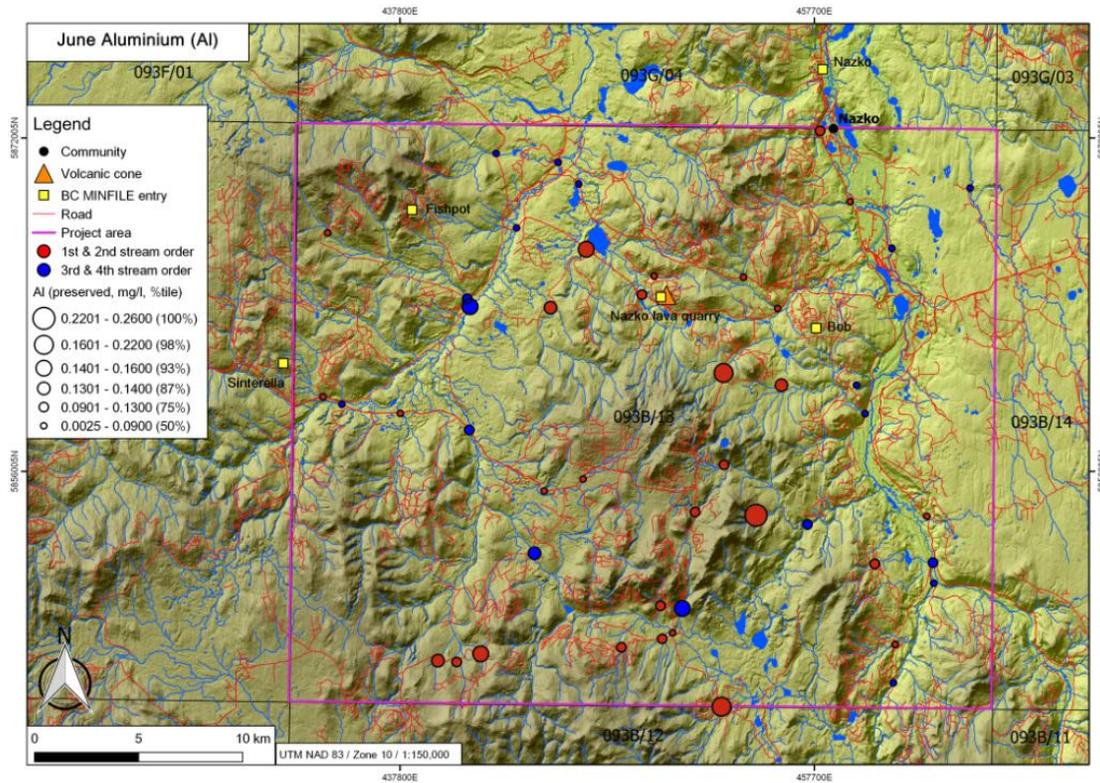


Figure 95. June photometer Al results.

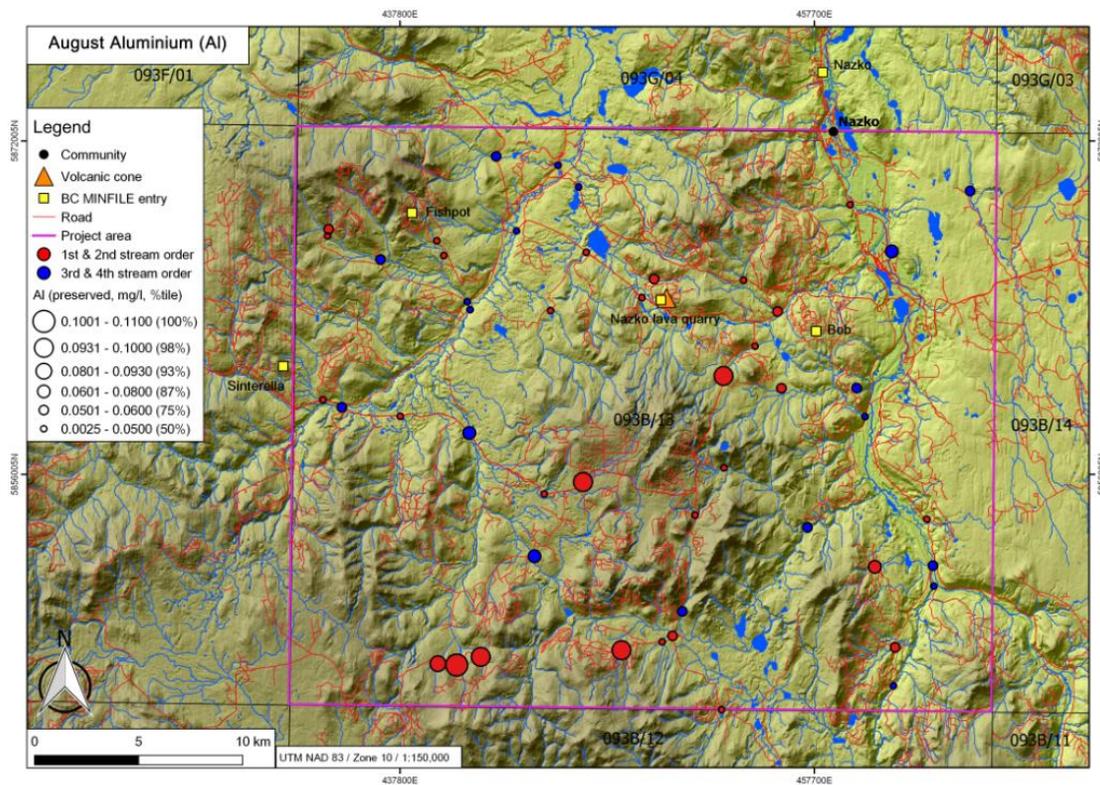


Figure 96. August photometer Al results.

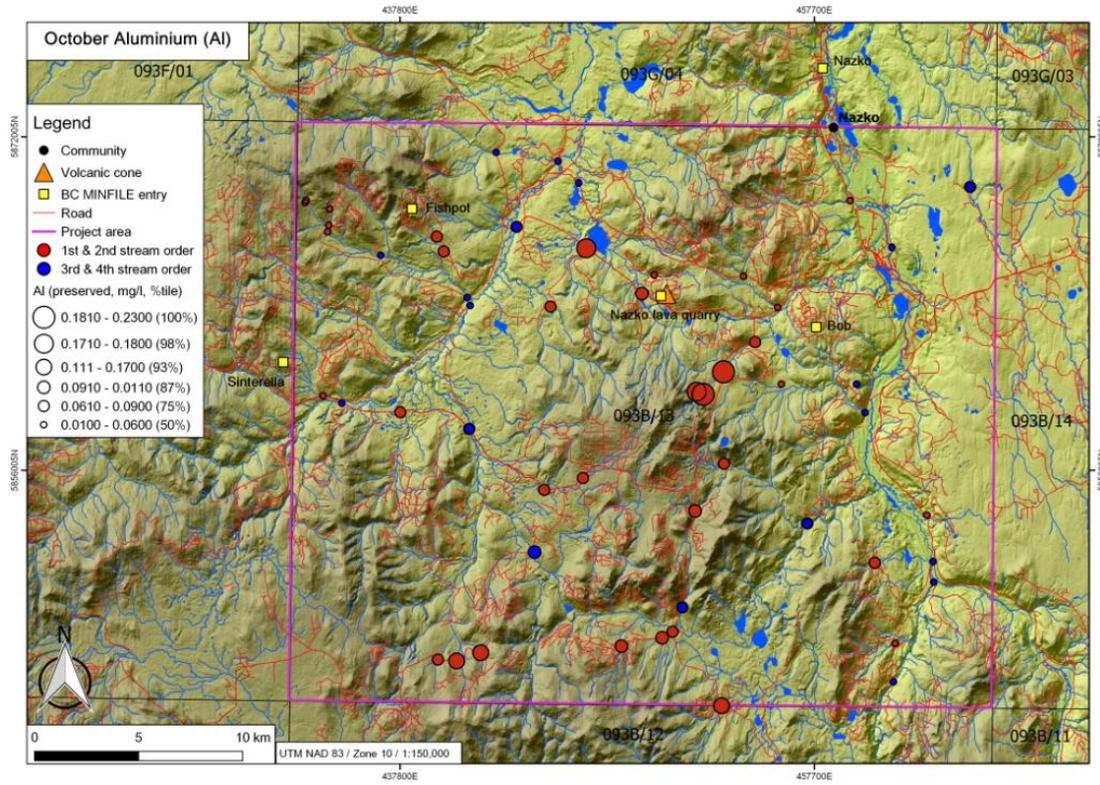


Figure 97. October photometer Al results.

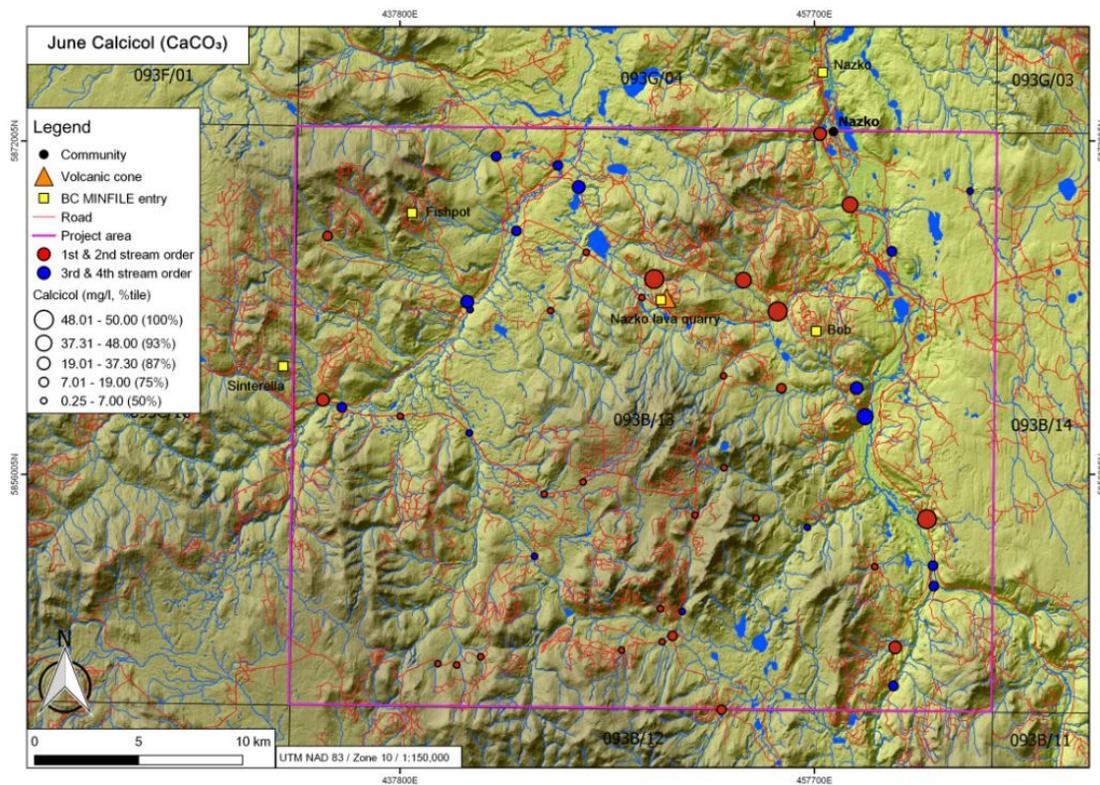


Figure 98. June photometer Calcicol (calcium hardness) results.

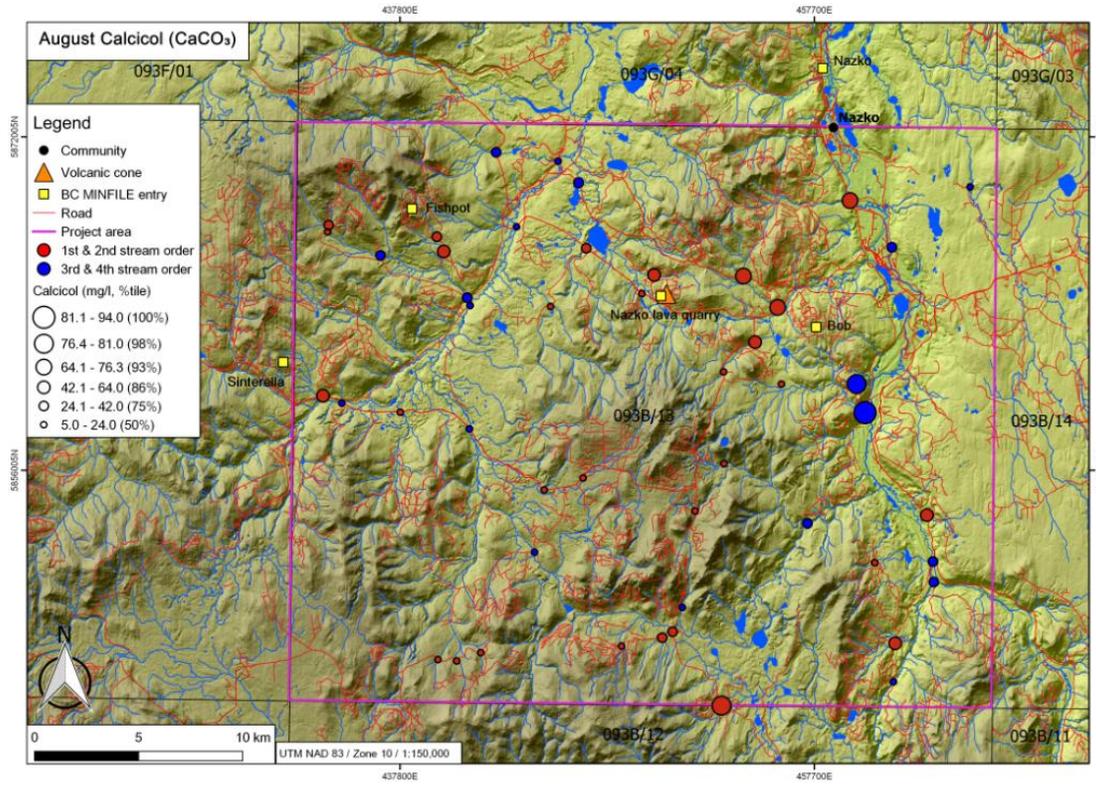


Figure 99. August photometer Calcicol (calcium hardness) results.

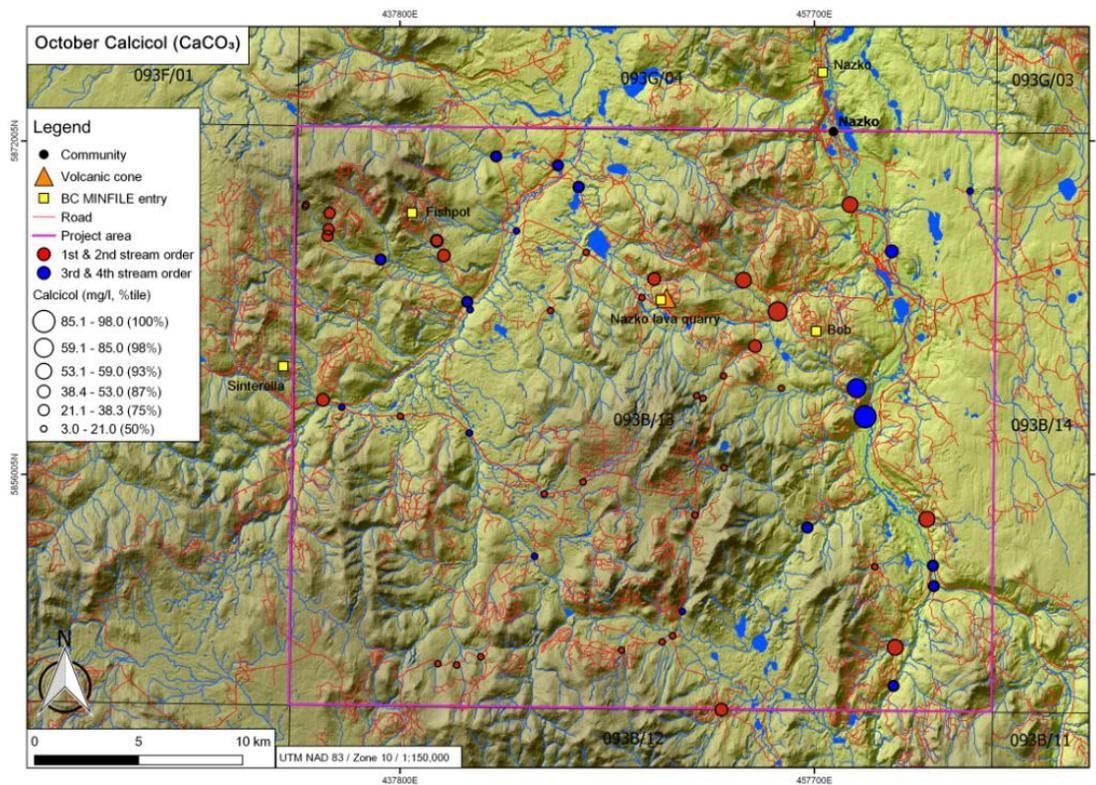


Figure 100. October photometer Calcicol (calcium hardness) results.

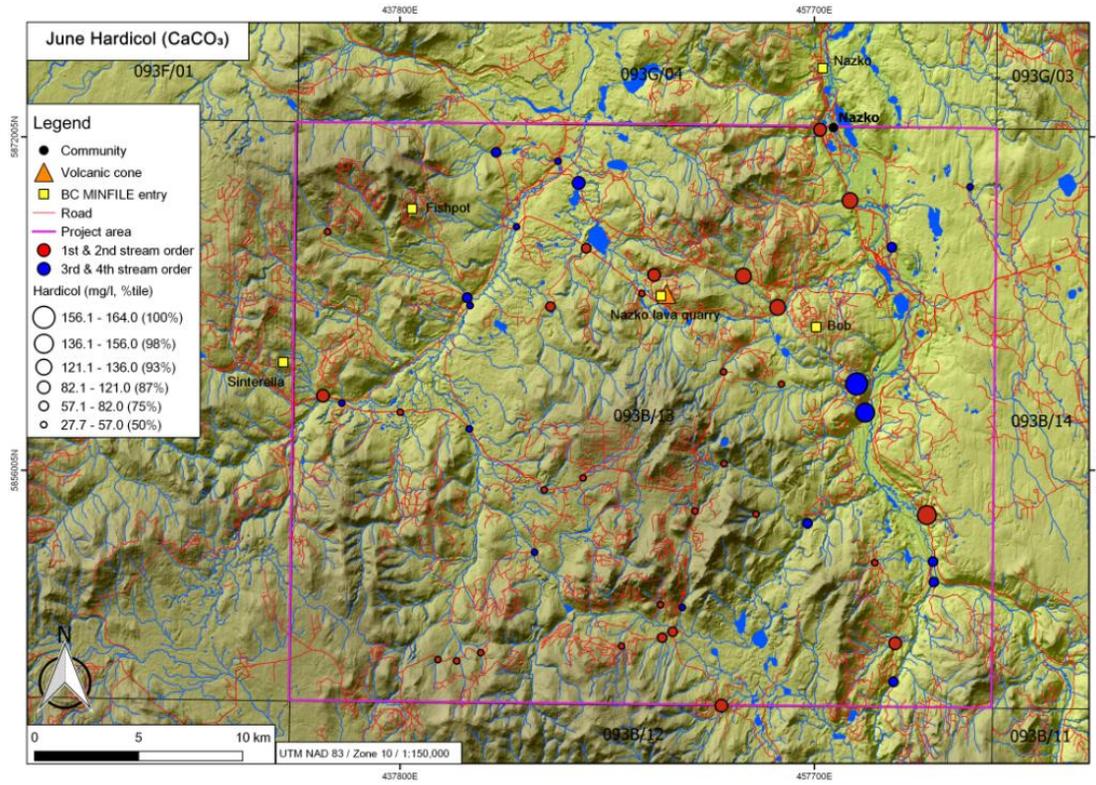


Figure 101. June photometer Hardicol (total hardness) results.

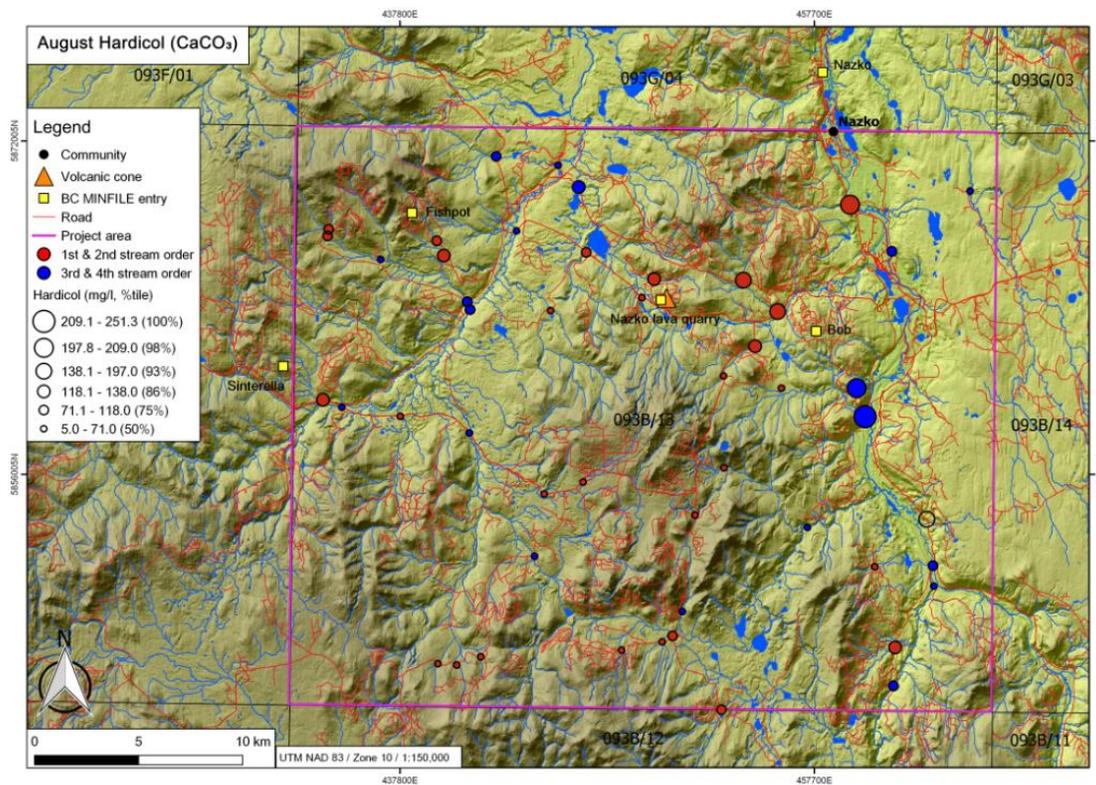


Figure 102. August photometer Hardicol (total hardness) results.

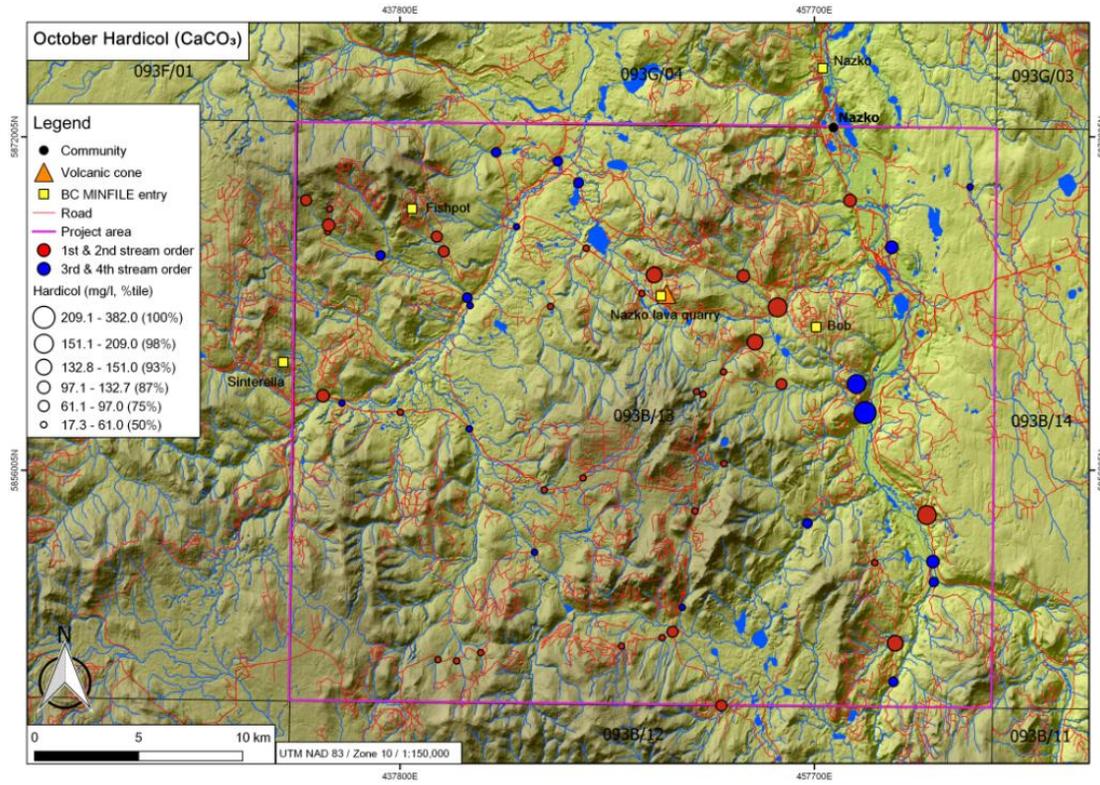


Figure 103. October photometer Hardicol (total hardness) results.

Potassium

Potassium (Figure 104 to Figure 106) shows a good correlation with alkalinity pH, Calcicol, Hardicol and Mg. It displays consistent concentrations between the seasons (median of 3.0 mg/l to 4 mg/l) with a slight increase associated with periods of precipitation.

Magnesium

Magnesium (Figure 107 to Figure 109) correlates well with pH, Calcicol, Hardicol and K with consistent patterns observed between seasons. Some of the 1st and 2nd order stream locations may indicate the presence of springs or ground water influx (Yehia and Heberlein, 2015) in areas underlain by calcite-bearing basaltic rocks. Overall the Mg test, as outlined throughout the preceding sections, has been the most reproducible analyte in this study.

Manganese

Manganese results (Figure 110 to Figure 112) demonstrate good correlation with the Zn and MoO₄ at the southern border of the map area. Maximum concentrations gradually increase, but only very little (0.003 mg/l to 0.007 mg/l).

Silica

Silica (Figure 113 to Figure 115) also displays consistent patterns between seasons. However, values are slightly more elevated in June, and decrease through August and October.

Sulphate

Elevated SO₄ (Figure 116 and Figure 117) correlates well with the Bob and Fishpot showings. It also correlates well with other locations that had elevated commodity analyte values such as the three locations at the southeast corner of the study area. Results are quite encouraging, considering the low concentrations recorded. Sulphate is an important indicator of sulphide weathering and the results show that, even at such low concentrations and variable weather conditions the photometer analysis is able to detect possible evidence of sulphide mineralization.

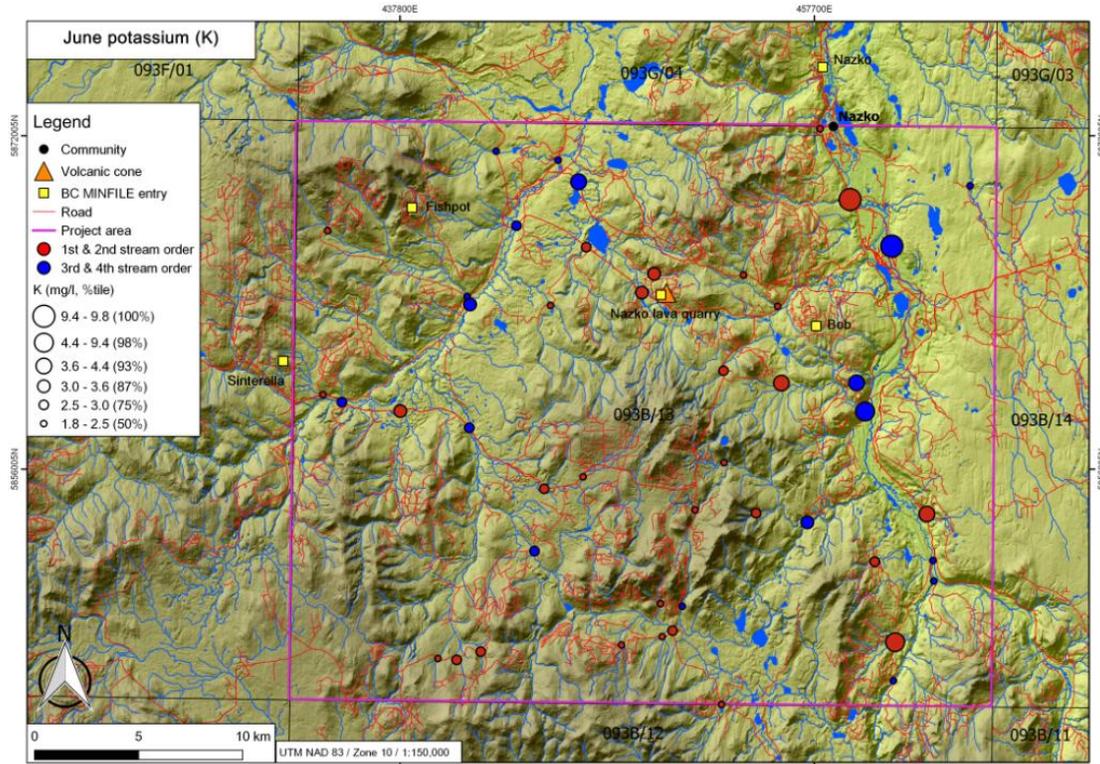


Figure 104. June photometer K results.

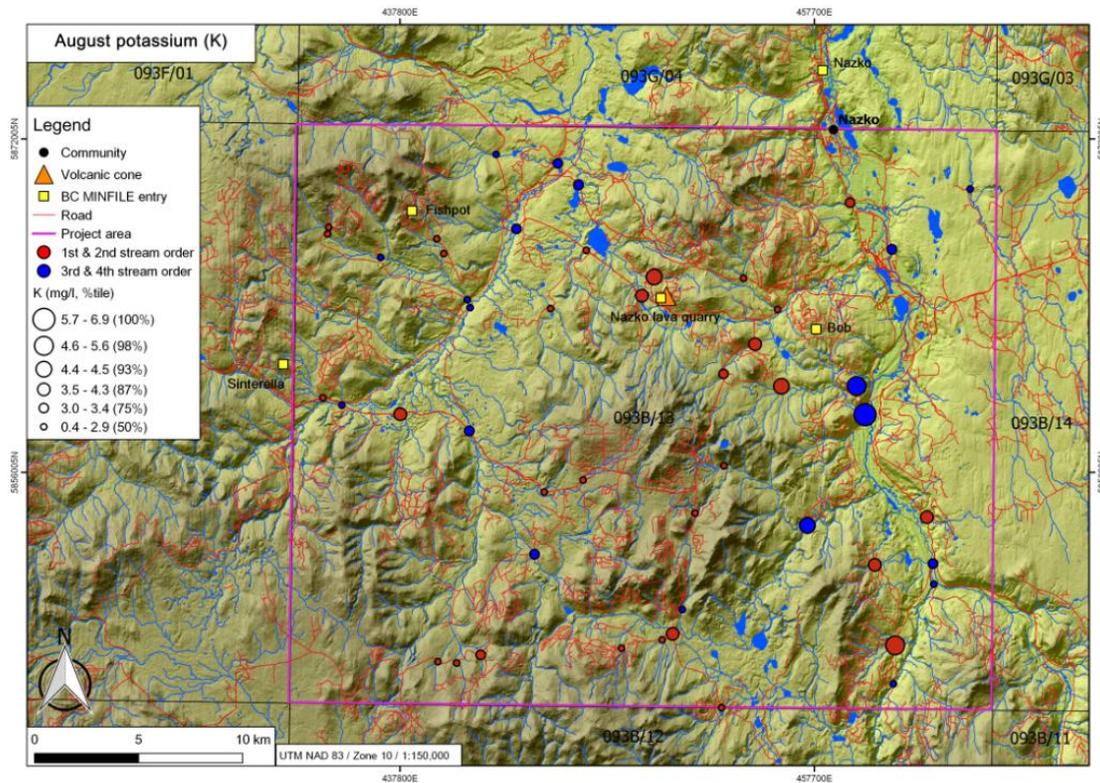


Figure 105. August photometer K results.

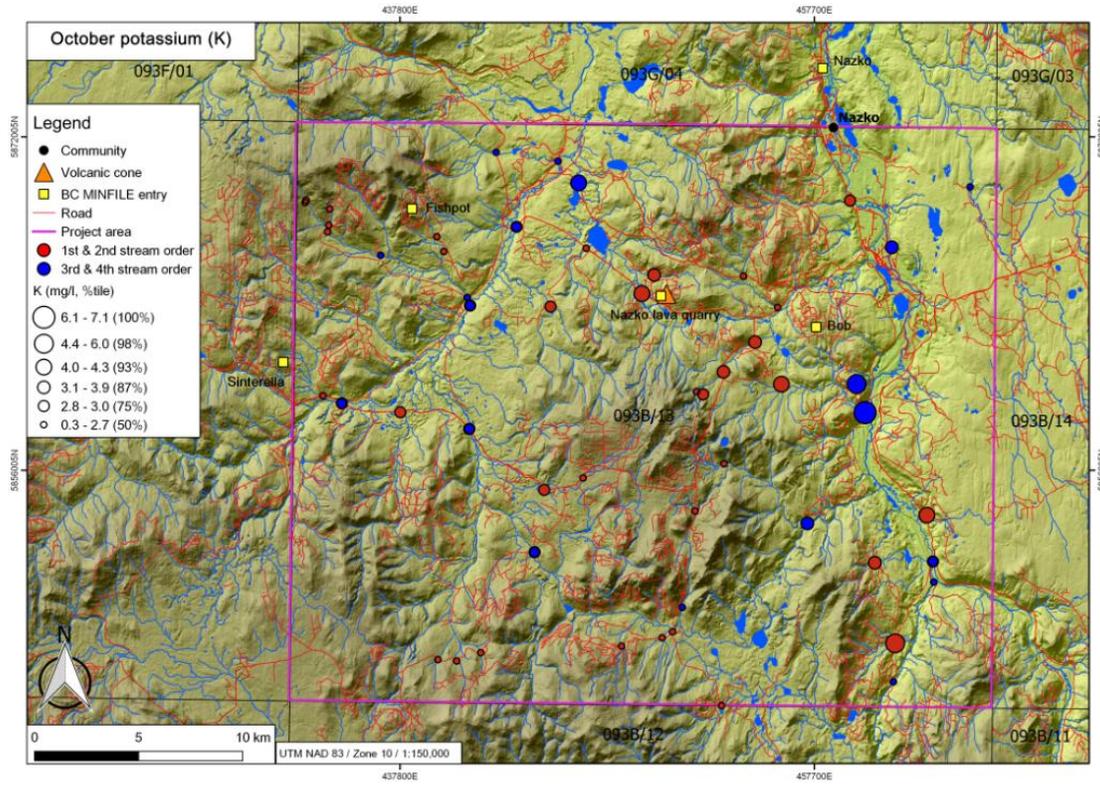


Figure 106. October photometer K results.

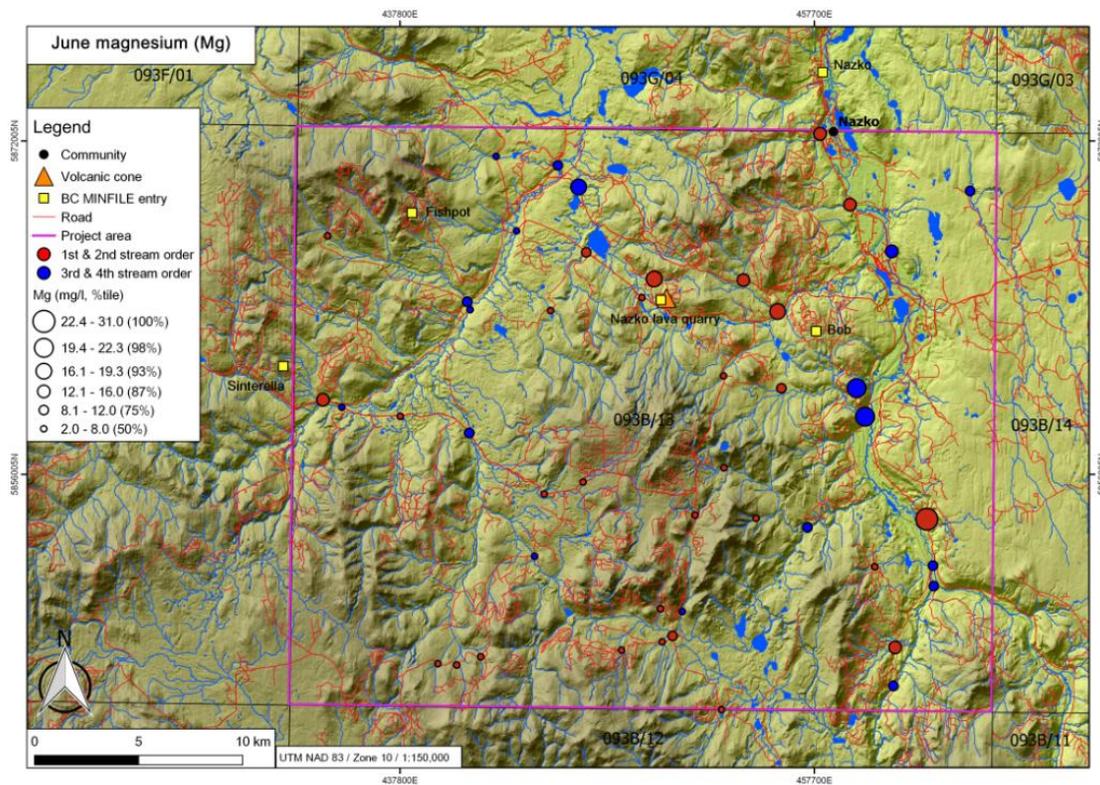


Figure 107. June photometer Mg results.

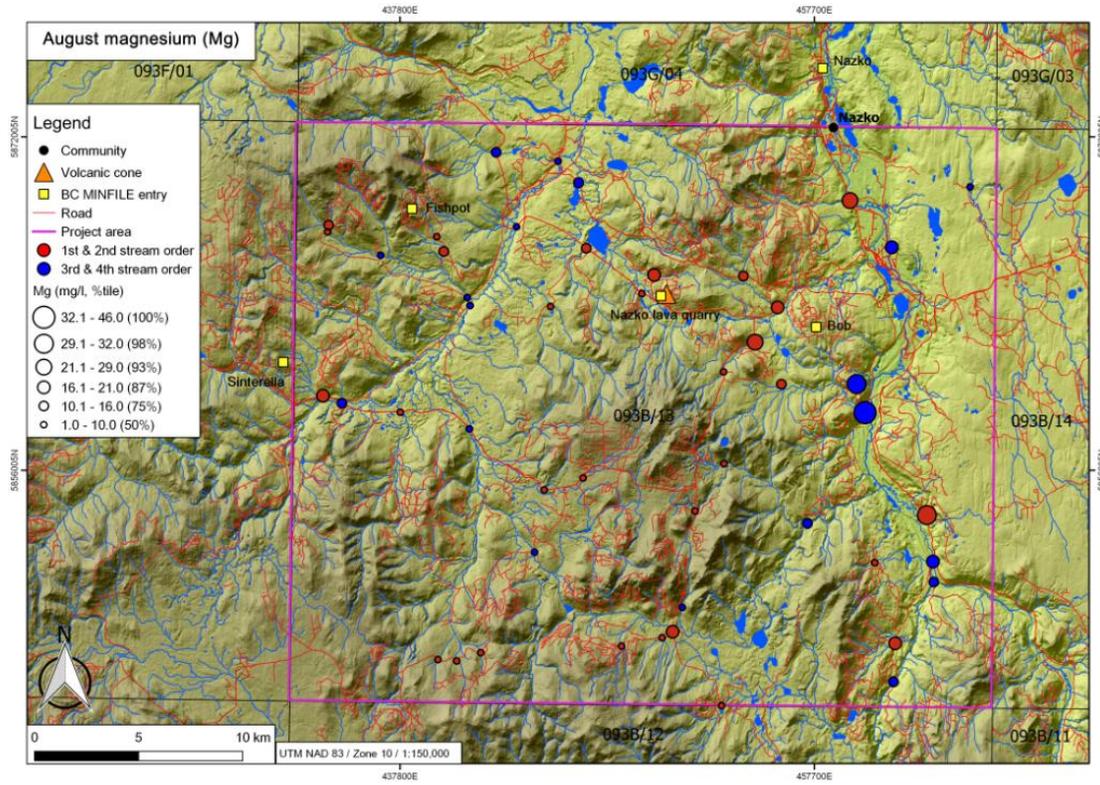


Figure 108. August photometer Mg results.

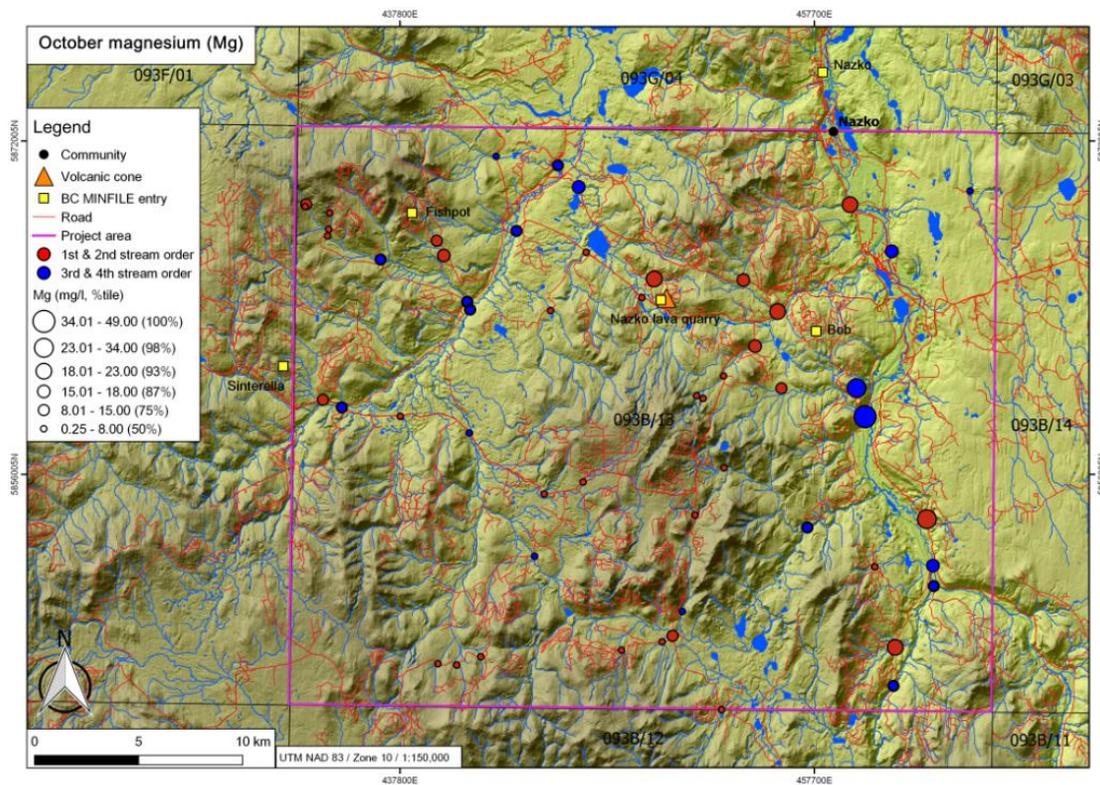


Figure 109. October photometer Mg results.

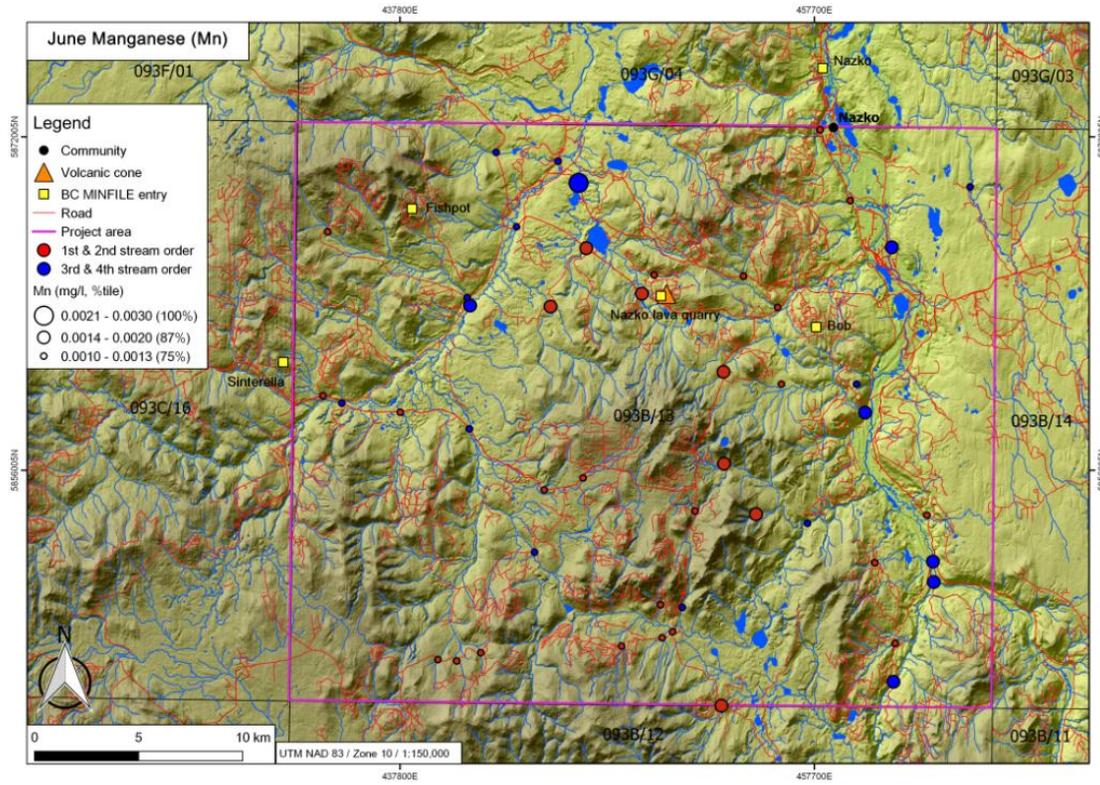


Figure 110. June photometer Mn results.

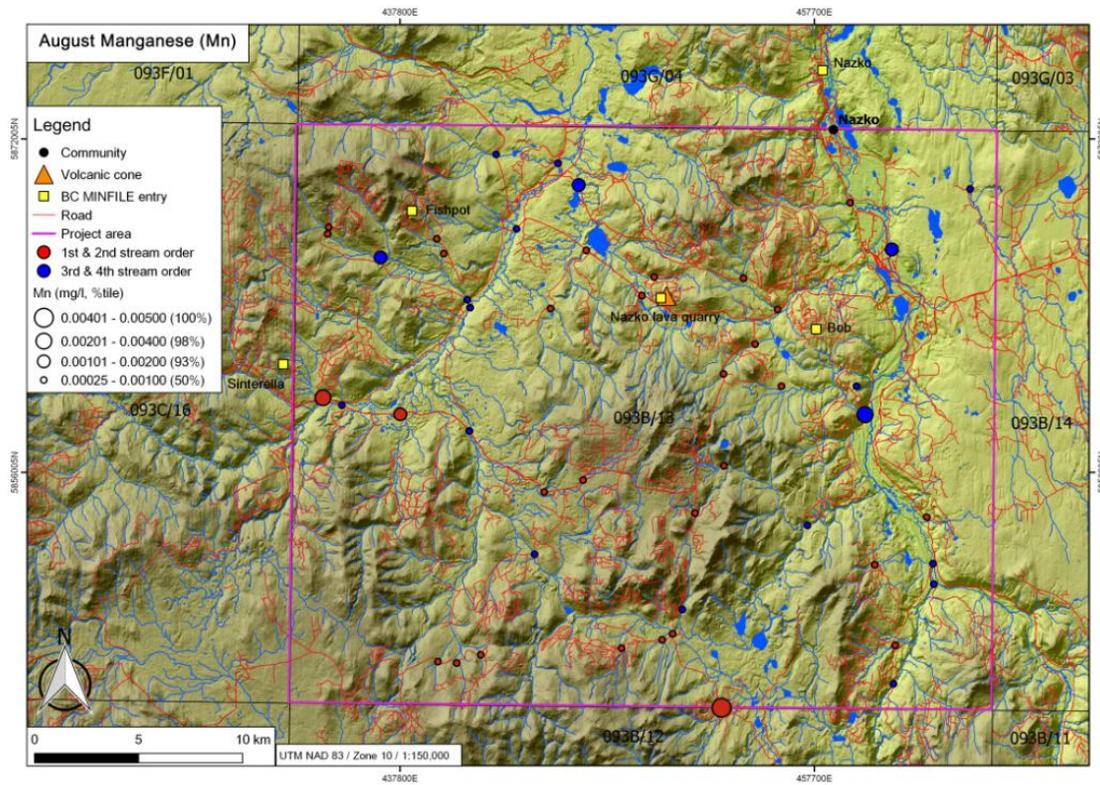


Figure 111. August photometer Mn results.

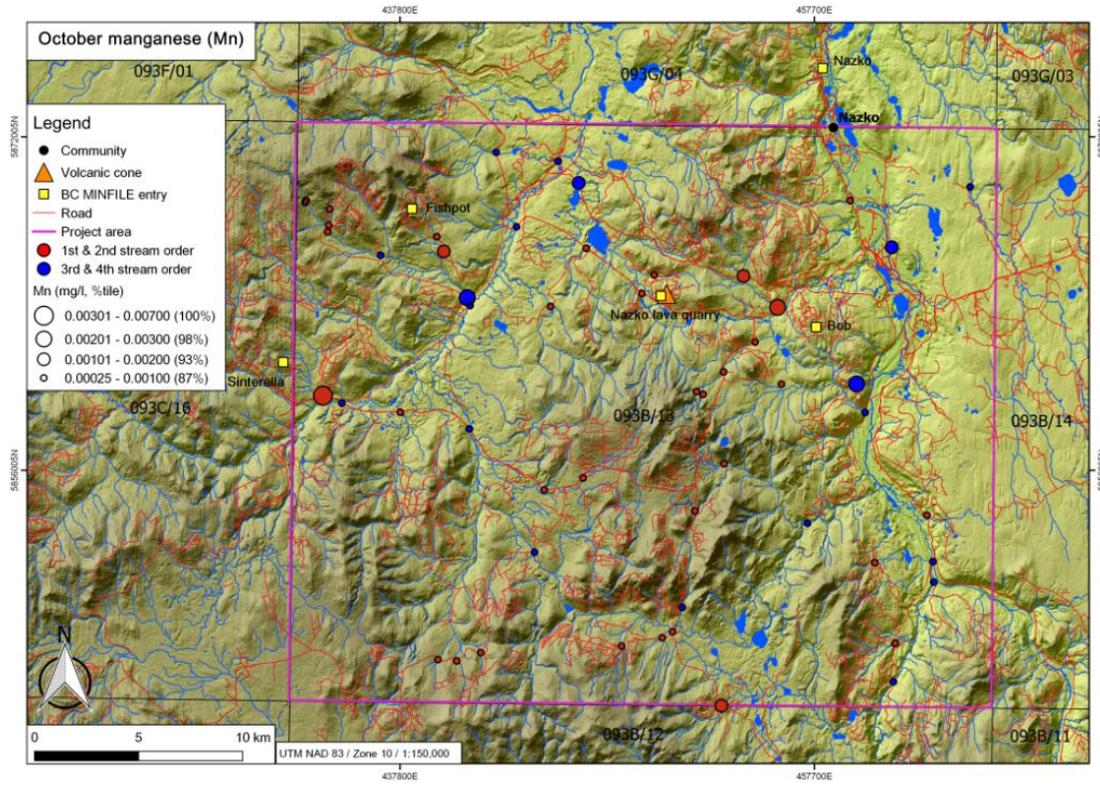


Figure 112. October photometer Mn results.

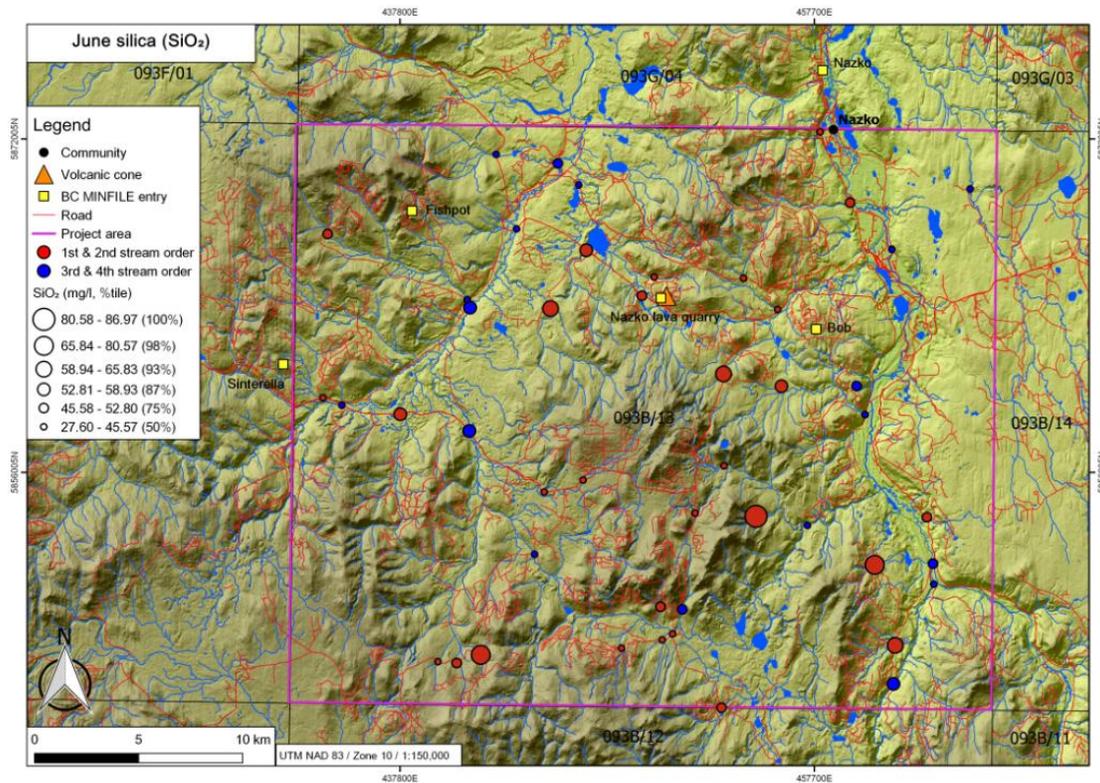


Figure 113. June photometer SiO2 results.

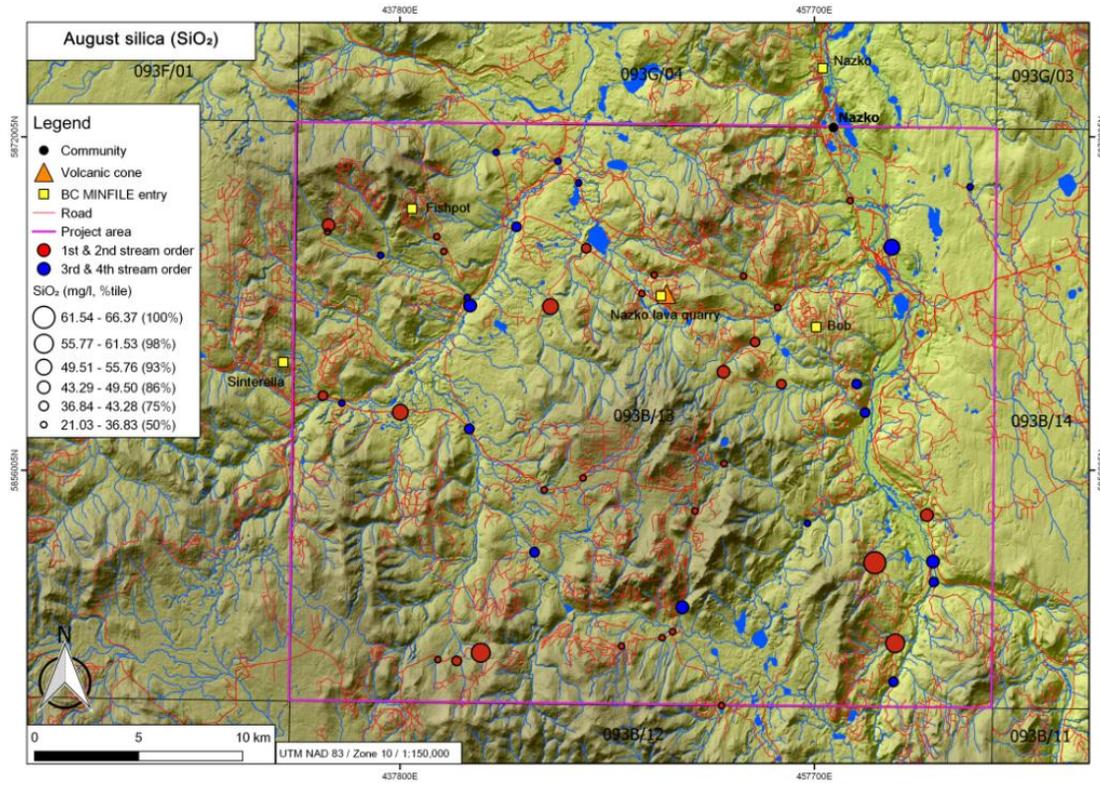


Figure 114. August photometer SiO₂ results.

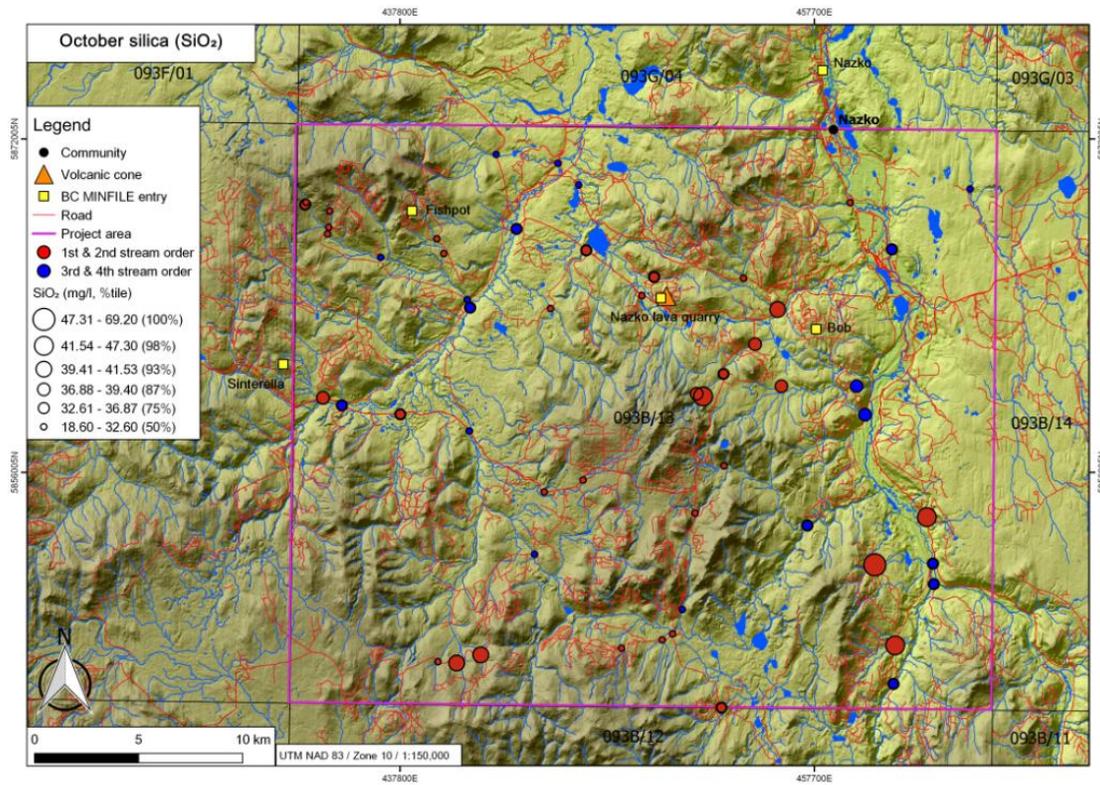


Figure 115. October photometer SiO₂ results.

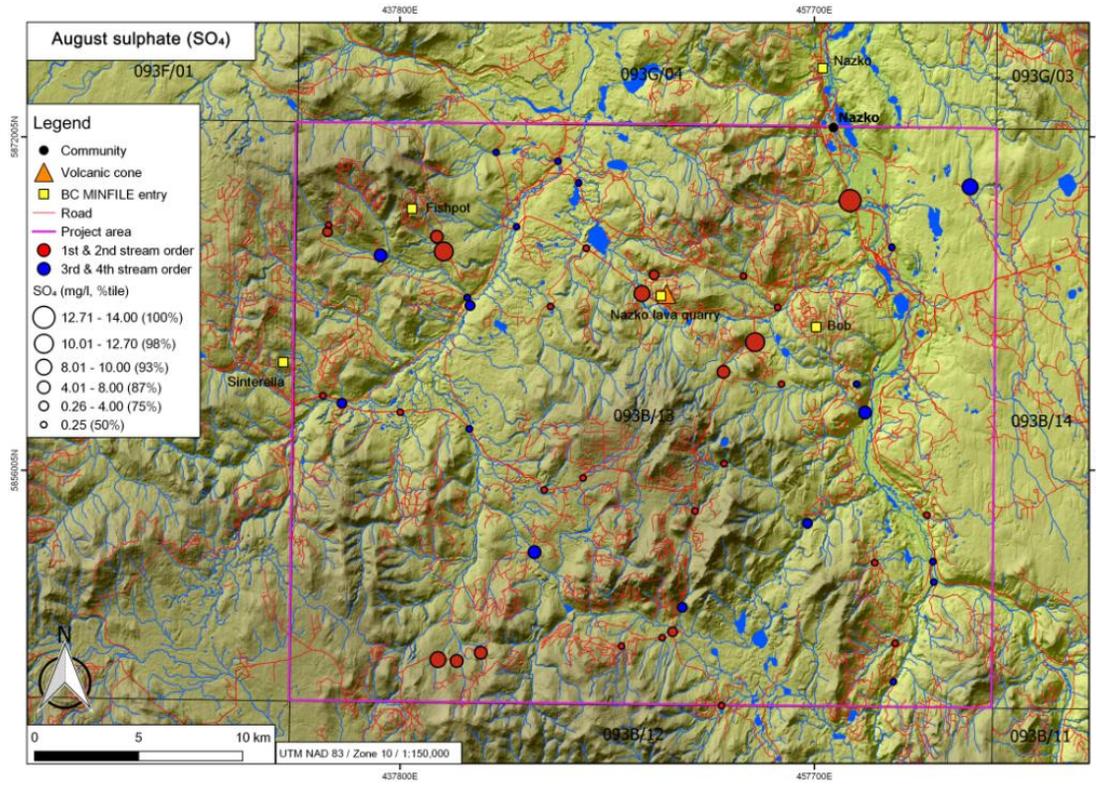


Figure 116. August sulphate photometer analysis.

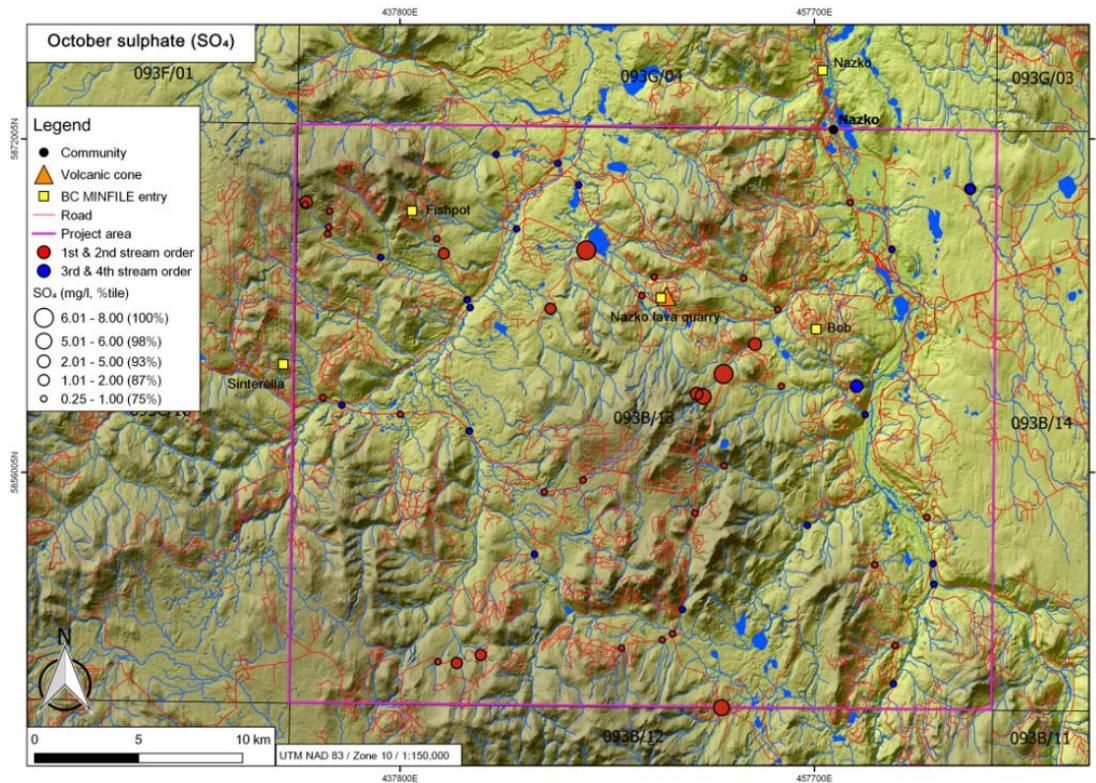


Figure 117. October sulphate photometer analysis.

Discussion

The first aim of this project was to provide regional-scale hydrogeochemistry data to supplement existing TREK datasets. Although some issues were encountered initially with the instruments, the results demonstrate that hydrogeochemistry is a viable tool for geochemical surveys in this surficial environment. The elevated Cu, As and SO₄ concentrations in proximity to Bob and Fishpot not only highlight the showings but also draw attention to other areas where mineralization may be present. At least two additional locations were identified that are worthy of further investigation (Figure 118). This is an example of how hydrogeochemistry can provide indications of mineralization and potentially expand the size of a target. However, it is also sensitive to other factors such as bedrock geology, overburden type, precipitation and weathering rates.

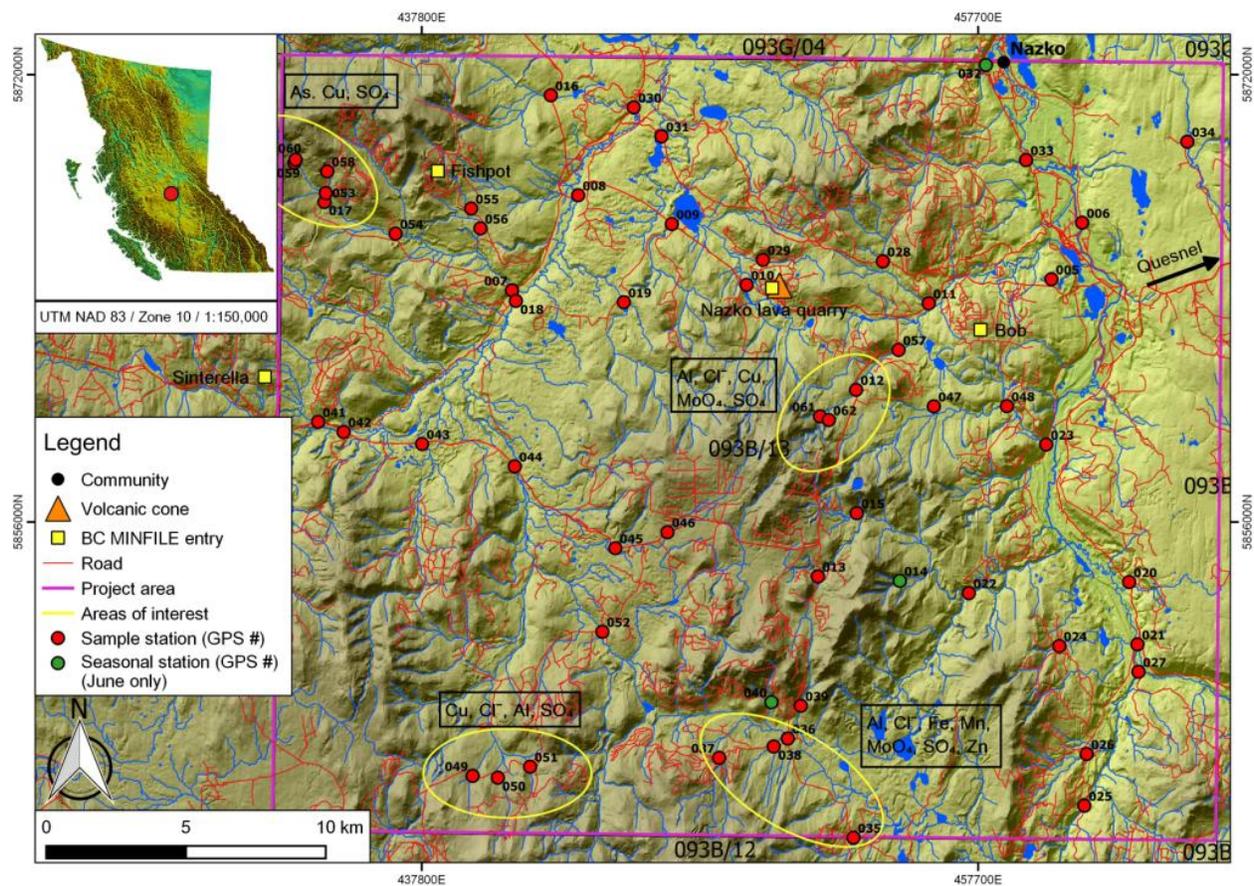


Figure 118. Hydrogeochemical anomalies.

Another objective was to continue examining the practicality of using portable devices for real-time field-based water surveys, this time at a more regional scale than our previous study. The results presented here show that the photometer and PDV can produce rapid and meaningful analyses for a suite of anions and cations at relatively low cost when compared with conventional laboratory-based methods.

Both in August and October, when time permitted, follow-ups were performed in selected areas, and analyzed while in the field. This is a considerable advantage over traditional laboratory based surveys, where results may not be available for sometimes several weeks. Even during traditional regional surveys, the ability to make decisions in the field for areas of interest is a valuable consideration in cost and time saving, which in turn improves exploration decision making.

The low detection limits for some analytes provides sufficient contrast and sensitivity to detect geologically meaningful patterns. Detection limits can be as low as single digit mg/l level for both devices. Another advantage of the photometer is the capability to perform error correction during a survey. Issues with sampling or analysis can often be identified and corrected on the same day.

Another advantage of the photometer is its ability to perform total Cu analyses in the field. The sensitivity of Cu to weathering and rainfall makes the test a valuable one, as concentrations in dissolved tests, which are partial analyses, may not be sufficient to allow for identification of potential targets.

Sample Collection and Density

One of the main lessons learned from this study is that sample filtration is not necessary. As both the photometer and PDV test for dissolved constituents, no filtration is needed (except for 10 ml for the photometer blank test). This provides the advantage of reducing sample collection time down to minutes. This was especially evident where there were highly turbid conditions and laboratory samples collected. Even using the filter wafer with a 250 ml container and hand pump (not syringe apparatus) filters had to be replaced numerous times which was time consuming. The issue was compounded during colder temperatures where filters ripped due to the cold and pressure, and sample collection had to be restarted.

The advantage of sampling 1st and 2nd order drainages is evident from the results above with some consistency and correlations between the various analytes measured in water at different seasons. The time and cost advantage of this methodology does allow reliable detection of analytes in 3rd and 4th order drainages. The 3rd and 4th order drainage water chemistry may provide insight into weathering conditions and dispersion (as with the As result at station 007 for example) but data analysis should be treated separately.

An additional advantage is the ability to increase sample density in response to results produced in the field. Traditionally average sample density for RGS is 1 sample/13 km². Photometer - PDV methodology in various situations could increase the density considerably, as long as density is consistent, thereby improving mineral detection and improving data interpretation, as well as identifying ground water sources and optimal sample locations for later laboratory analysis. Increasing sample density would also allow analyte detection at times of higher dilution.

Sample Analysis

For this survey an average of five samples per day were collected and analyzed. As efficiency and experience of the team improved, the speed of analysis increased.

The number of available reagents provides a good suite of analytes for testing when compared to laboratory analytical packages. The ability to add additional tests for the photometer and PDV is available. The advantage for this methodology is the ability to select relevant tests, which could decrease analysis time and cost. The tests can provide screening for optimal sample locations for laboratory analysis and type of suites (comparable to portable XRF unit usage).

The issue regarding the effect of turbidity on the photometer readings was a concern, but it was identified and appropriate steps were introduced, both in analysis and QAQC, to minimize its impact on the data. The issues experienced with the two sets of tests performed with the PDV were resolved and data is considered reliable, but the experience has shown that careful planning should be made well in advance for proper analysts and training selection.

Orientation Surveys

Prior to routine sample collection an orientation survey should be an integral part of survey planning. The orientation survey in this study was not successful in establishing the sample collection methodology for the surveys, but was useful for sampler training and for identifying sampling and analytical problems prior to commencement of the main sampling campaigns. At the start of the Nazko area survey an orientation established a base station for monitoring water chemistry over time, the water sample collection method, instrument operation and calibration and identified background levels of key analytes in the water.

Reliability

As with the previous study, careful attention is paid to the accuracy and precision of the analytical results. Extensive analysis of calibration and standard data shows that the portable devices provide accurate data that can be used for interpretation.

The variability at low concentrations for some of the reagents is a concern; but with proper QAQC procedures many of the issues identified early in the study were corrected; for instance, the effect of the turbidity on ionic Cu. Also of concern were some of the concentration biases observed between the field and laboratory measurements. The high laboratory bias for Al, Fe and Mn and the photometer bias for F⁻ are still not sufficiently adequately explained due to the different methods used. Another area of concern is the apparent inconsistency between the laboratory and photometer turbidity and TDS measurements, although the cause for the inconsistency is due to the difference between the data collection and analytical methodologies.

Seasonal and Daily Variation

Considering the above average precipitation during the field season, results still provide a good understanding of how the analyte concentrations responded to varying precipitation. Unfortunately, our understanding of the effect of turbidity on the June results meant that important data for Cu, MoO₄ and SO₄ could not be produced for the early part of the study. Despite this issue, sufficient data was collected to provide an understanding of behaviour of some analytes. Some analytes (e.g. Fe, Mg, K, hardness), showed little variation between seasons. Others such as Cu, Mn and MoO₄ responded differently to changes in precipitation. Even though concentrations increased in October for these analytes, patterns did not change significantly between August and October. Concentrations could be sufficient to have provided the same results in July, and in the case of Cu (total) in June as well. For some analytes like SO₄, concentration decreased in October, suggesting that the best time to sample is mid-summer.

Base station measurements were valuable for monitoring the impact of daily and local rainfall on stream water chemistry. The base station data helped to identify the effect of dilution on the variation of such analytes as Al, Cu, Cl⁻ and MoO₄ and strengthened the interpretation of the data. Future water surveys should include a local hydrogeochemical base station for daily variation monitoring

Cost per Analysis

Labour cost for photometer analysis was \$57.09/sample. The additional cost for this study (compared to the last) is from the added PDV reagents, and an additional operator. Two operators were recruited, one for each device. Cost is a very conservative calculation based strictly on 208 samples. It does not include many additional tests and (or) experimentation performed, such as turbidity reruns, or added confirmation of Cu and MoO₄ tests in August and October. Cost for PDV was based on flat 1.3 conversion rate from \$US dollars. Shipping would have added additional cost to laboratory samples. A breakdown of costs is shown in Table 8.

Table 8. Summary of cost per sample.

Type	Photometer cost per sample	ALS Environmental cost per sample
Photometer reagents	\$10.36	
PDV reagents	\$5.32	
Analysis	\$57.09	
Environmental disposal	\$2.21	
Shipping		\$1.58 ¹
Total	\$75.98	\$229.17

¹Based on Canada Post Regular Parcel (2 business days) pricing.

Conclusions

Conclusions of this study to test a Field-Portable Photometer and Voltammeter for the analysis of water samples collected from streams over 500 km² over the Marmot Lake NTS map area are that:

- The photometer and PDV can produce rapid and meaningful analyses for a suite of anions and cations at relatively low cost when compared with conventional laboratory-based methods.
- The ability to forgo sample filtration for the portable devices testing improves sample collection time considerably.
- Elevated Cu and As were detected in water samples from streams draining the area surrounding two known mineral showings. Drainage from two other areas with no known sulphide mineralization has elevated Cu and SO₄, and is worthy of follow-up.
- Time and cost advantage of the methodology allows increasing sample density.
- An orientation survey is important to establish optimum field operating conditions and provide adequate training for PDV operations.
- A local hydrogeochemical base station is important for daily variation monitoring.
- For some of the analytes (CaCO₃, K, Mg, SiO₂) there is a good correlation between the results of the in-field and laboratory analysis.

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Digital Appendix

Includes the following spreadsheets:

- Field observations
- Analytical data
- Orientation survey analytical data