

# Geochemical Investigation of Halogens in Spruce Treetops and Integration with Existing Multi-Element Data from the Blackwater Region and TREK Project Area, Central British Columbia (NTS 093C, F)

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## Introduction

In 2015, Geoscience BC funded a helicopter-supported spruce-treetop sampling program at 1.5 km spacing on an offset grid, followed by multi-element analysis of twigs and needles, in the Blackwater region and TREK project area (Jackaman and Sacco, 2016) of central British Columbia (BC; Figure 1). The survey area has a thick vegetation cover, few lakes and a limited road network such that other surface geochemical-exploration methods would be very time-consuming and expensive.

Jackaman and Sacco (2016) published results from the analysis of 421 milled spruce-twig samples (dry tissues; locations shown in Figure 2); the needles from these same samples were also analyzed, but were first reduced to ash to concentrate elements prior to multi-element analysis by inductively coupled plasma–mass spectrometry (ICP-MS) with an aqua-regia digestion. Surplus needle ash was available for further analytical work and, since the analysis method for detecting halogens in similar materials was being developed under another project (Heberlein et al., 2017a, b), the opportunity was taken to use these archived samples to further develop the analytical methodology and add another layer of data to the original datasets. The purpose of the sample reanalysis was to examine the distribution patterns of halogens at a regional scale of sampling to determine if these volatile elements might identify geologically meaningful patterns and provide confirmation of some subtle element enrichments identified in the original survey datasets.

Fluorine is the most reactive element in the periodic table, forming compounds with every element except the noble gases He, Ne and Ar. It is also the most electronegative element. The remaining halogen elements (i.e., Cl, Br and I) are also highly reactive but less so than F. All four halogens

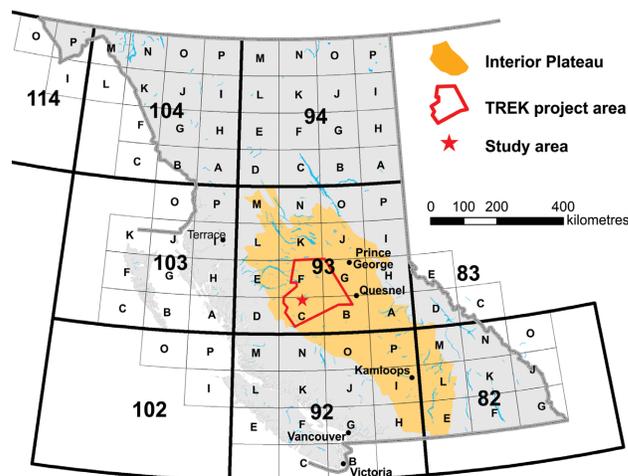
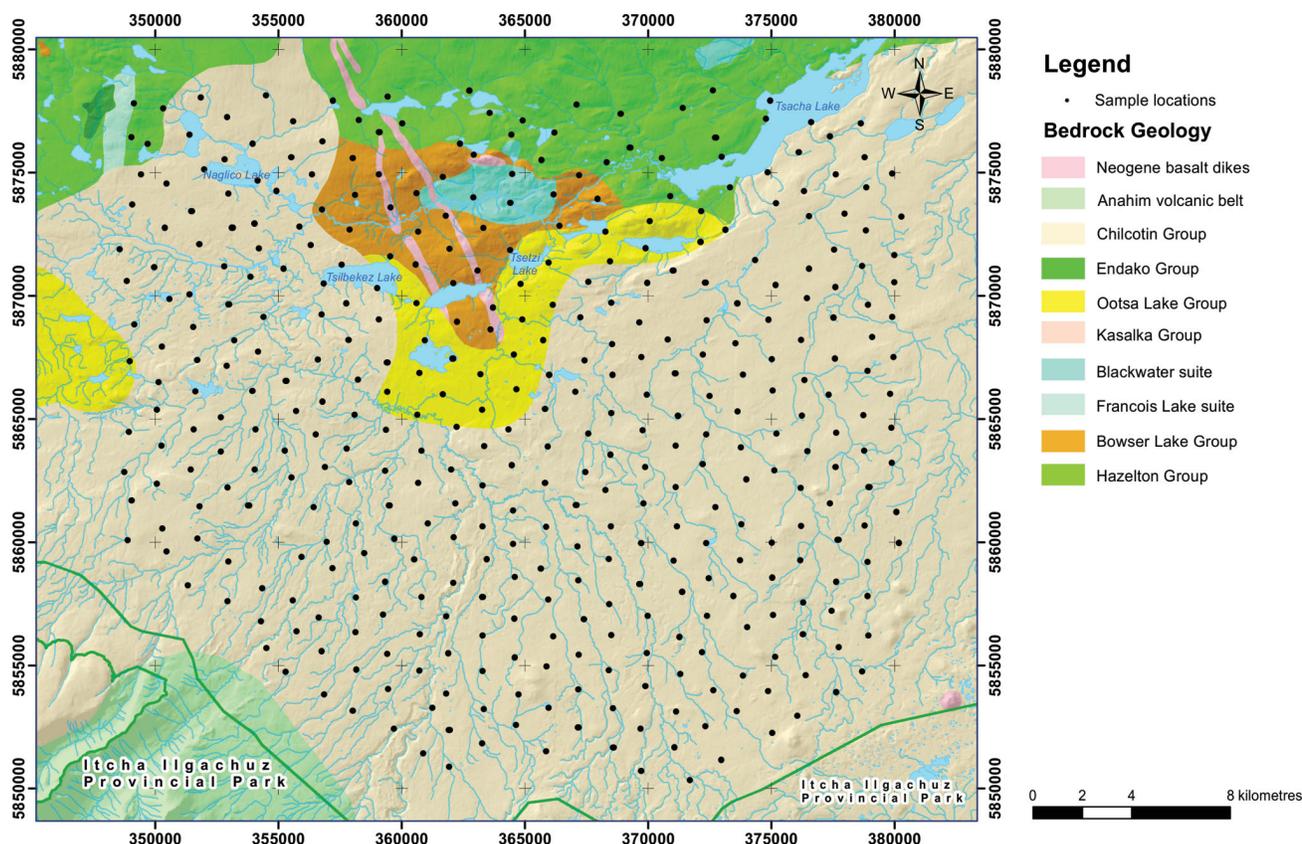


Figure 1. Biogeochemical survey area, Interior Plateau, central British Columbia.

are particularly enriched in differentiated magmas; the hydrothermal fluids and volatile compounds derived from them play an important role in the mobilization and transport of metals in ore-forming systems. In the primary environment, they reside in a variety of hydrous minerals including micas, amphiboles, scapolite, topaz and apatite. Elevated halogen concentrations are also documented in high-salinity liquid phases and daughter minerals in fluid inclusions in igneous and hydrothermal minerals (Kendrick et al., 2012; Kendrick and Burnard, 2013). On exhumation and weathering at the earth’s surface, the host minerals break down either mechanically or chemically and release the halogens into the surficial environment. Being highly soluble in water, they are rapidly transported through drainage systems to the ocean as anions.

In mineral exploration, there are case histories that demonstrate positive responses of all these elements to zones of concealed mineralization (Billings and Williams, 1967; Al Ajely et al., 1985; Lavery, 1985; Ridgway, 1989, 1991; Ridgway et al., 1990; Trofimov and Rychkov, 2004). However, other than some Geoscience BC research projects carried out in recent years (Dunn et al., 2007; Bissig et al.,

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**Figure 2.** Geology of survey area with treetop sample sites; the green lines indicate park boundaries. Geological units after Angen et al. (2017).

2013; Heberlein et al., 2013; Heberlein and Dunn 2017a, b; Heberlein et al., 2017a, b) and a trial study on a limited dataset, using ashed Douglas-fir needles (Dunn and Thompson, 2009), these methods have seen little or no application to the exploration for minerals in the extensively covered terrains of BC or elsewhere.

A good example of a large geochemical footprint of F surrounding a volcanogenic massive-sulphide ore deposit is at Crandon (Wisconsin), where the halo extends approximately 320 m into the footwall rocks and at least 220 m from the ore. Other base-metal deposits also exhibit F haloes: in Arizona, for example, the United Verde deposit has a F enrichment in footwall rocks of at least 650 m from the ore and distinct F haloes are present around smaller deposits in New South Wales (Lavery, 1985). Similarly, Church and Barakso (1990) reported in a study of about 1700 rock samples in the Buck Creek area of BC:

*“Fluorine is ubiquitous in the rocks of the map area and rarely falls below 100 ppm. At the Equity mine fluorine is depleted over the ore zone. A weak discontinuous halo rising above 1000 ppm fluorine can be interpreted as surrounding the deposit.”*

With these examples in mind, ALS-Geochemistry analytical laboratory (North Vancouver, BC) has further devel-

oped analytical methods enabling scientists to investigate the halogen responses in surface media near base-metal and gold mineralization in BC (Dunn et al., 2007; Heberlein and Dunn, 2017a, b; Heberlein et al., 2017a, b) with a certain measure of success. The last of these studies resulted in ALS developing their HAL-01 and HAL-01a methods and marketing them at a lower cost than had previously been possible. However, further analytical refinement of the methods was still required and is presented in this summary.

### Relevance to the Exploration Community

This study is designed to provide the mineral-exploration community with additional layers of geochemical data from the analysis of tree tissues that could contribute to the identification of zones of metal enrichment possibly deriving from deep-seated or covered mineralization and/or could reveal structural elements and rock types likely to provide a focus for exploration efforts. This is based on the rationale that the halogen elements are commonly instrumental in the emplacement of metal deposits and generate broader haloes of enrichment than the metals themselves. Refinement of the analytical methodology leads to more accurate and precise data, and potential lowering of costs,

thus making these methods more attractive and practical to the exploration community.

## Survey Area

The following description is taken largely from Jackaman and Sacco (2016), in which the authors describe the survey area as characterized by gentle, north-facing slopes that are blanketed with glacial drift and dissected by streams that flow into the lowland. Interspersed throughout the 1000 km<sup>2</sup> survey area are stands of lodgepole pine (*Pinus contorta*), white spruce (*Picea glauca*) and Engelmann spruce (*Picea engelmannii*). A hybrid species of white and Engelmann spruce (known as Interior spruce) is also common in the central Interior. Fortunately, from several previous studies, the lead author was able to determine that these spruce species have very similar chemical characteristics. Wetland features and sedge-grass meadows are common. There is evidence of beetle-killed pine, recent forest fires and regeneration from previous forest fires. Few access roads extend into the survey area, but forest service roads are located to the north and east.

The survey area is underlain by Hazelton Group and Ootsa Lake Group rocks, and Chilcotin Group volcanic rocks. Several developed prospects that contain Au, Ag, Zn, Pb and Cu mineralization are located in the region. The Blackwater-Davidson intermediate-sulphidation epithermal Au-Ag deposit (NTS 093F/02; MINFILE 093F 037, BC Geological Survey, 2019) is located 15 km northeast of the survey area and the 3Ts polymetallic Ag-Pb-Zn±Au deposit (NTS 093F/03; MINFILE 093F 068) is situated on the northern survey boundary. Previous work at the 3Ts deposit established a positive response of halogens to concealed mineralization (Dunn et al., 2007). No recorded mineral occurrences exist within the survey area south of the West Road (Blackwater) River and lack of outcrop has resulted in interpretation (from airborne geophysics) of the underlying bedrock in most of the survey area as being Chilcotin Group volcanic rocks (Figure 2).

## Sample Collection and Analysis

### Sampling and Sample Preparation

Details of the sampling program are given in Jackaman and Sacco (2016), in which it is stated that:

*“Field survey methods, sample preparation and analysis protocols guiding the 2015 biogeochemical survey were based on previous field surveys, orientation investigations and detailed research (Dunn, 1995, 2007). During a six-day period in June 2015, a 1000 km<sup>2</sup> area was surveyed using predetermined flight-lines along an offset grid with 1500 m spacing between sample sites. A total of 421 side-branch samples, comprising 1 kg of twigs, needles and cones, were systematically collected near the tops of 399 healthy spruce trees (Figure 3).*

*The target spruce trees were healthy, 80–100 years old, 20–25 m tall and commonly extended 2–3 m above a lower canopy of lodgepole pine, which typically showed effects of the mountain pine beetle infestation. A recent forest fire in the northern part of the survey area and several immature patches of forest regeneration limited the availability of spruce for a small number of the predetermined sites.*

*Navigation along the predetermined flight lines and the recording of sample site location co-ordinates were completed using tablet based mapping and GPS computer programs.”*



**Figure 3.** Spruce-treetop sample collection in central British Columbia, showing sampler secured to the helicopter with a safety harness and lanyard. Photo courtesy of E. Banner.

After oven drying at 60°C, the needles were removed from the twigs and a 50 g split of dry needles (which were the only tree tissues used in the current study for determining the halogen contents) was reduced to ash at 475°C, generating 2–3 g of ash. A 0.25 g aliquot of the ash was analyzed for 53 elements plus rare-earth elements by ICP-MS following aqua-regia digestion. Consequently, plenty of ash remained for refinement of methods used for halogen analysis; all the original packets of ash were therefore obtained from W. Jackaman and sent to ALS for further method development, after which all 421 samples were analyzed for F, Br, I and Cl.

## Method Description

The information on which this section is based has been provided by ALS.

‘Super Trace F, Cl, Br, I’ is a recently developed method, which ALS describes as the ME-HAL01a method, that has proven to be suitable for ashed vegetation. After reducing vegetation to ash at 475°C for 24 hours, samples are leached with hot de-ionized water (90°C) and analyzed by a combination of ion chromatography and ICP-MS.

Method precision was determined using ashed vegetation reference materials. The aliquot weight was optimized (0.5 g) to improve recovery and precision for all halogen elements. Table 1 shows concentrations of halogens obtained from 0.25 and 0.5 g aliquots of VEG-V4a (balsam fir-needle ash) and VEG-V8a (spruce-needle ash). It demonstrates very good precision and shows that there are higher F recoveries from the 0.50 g than from the 0.25 g samples.

A comparison of F results obtained by the Super Trace method and traditional ion-selective electrode analysis indicates that the Super Trace method (0.50 g) consistently recovers about 50% of the total F (the water-soluble component) yet is suitable for exploration targeting. Work is ongoing on the percentage recoveries of Br, Cl and I.

## Multi-Element Analysis and Reanalysis of Selected Samples

The original multi-element datasets included a comprehensive suite of control samples and repeat analyses for defining the analytical quality. These results are detailed in

Jackaman and Sacco (2016), who noted that some elements (e.g., Au and Ga in ashed needles) exhibited slightly elevated values along sample sequences. The concentrations of these elements were generally very low and may reflect detection-level artifacts related to sample weights and/or heterogeneity (J. Sader, pers. comm., 2016). Of concern was a trend of elevated Au values in the western part of the survey area. Investigation of the original data established that this sequence was confined to one particular test-tube rack of samples, indicating that a slight difference in the digestion procedure might have been the cause. As a follow-up to this problem, the original analytical laboratory, Bureau Veritas Minerals (Vancouver, BC), has been asked to reanalyze the ash samples in question to assess the reproducibility of the anomalous results. A total of 22 samples were sent to the laboratory, including two control samples. Results can be summarized as follows:

- After storage of ash in packets for four years, the data for most elements were very reproducible, confirming that the ash samples retain their integrity over time.
- The Au, As and Sb data did not reproduce well, largely due to the very low concentrations of these elements in the samples (As and Sb have therefore been omitted from comparisons of trends with the halogen data); however, given the low levels, the Au values nevertheless appear to be reproducible for all samples except the problem samples, which returned values below the lower detection limit and, consequently, the original analytical values for Au in this short sequence of samples have been replaced by the new results (of relevance is that the results from some of the reanalyzed samples requested by W. Jackaman were very similar to the latest results, thereby confirming that the original values for Au in a short sequence of samples were suspect and should not be relied upon).
- Other elements that showed a good correlation on reanalysis, but were lower after four years, were Li and Sc, whereas the opposite occurred for Mo (higher after four years).
- The Sb values were higher on the reanalysis and the Te values lower, which suggests that these data should be treated with caution.
- Since analytical precision for this study is of more relevance than analytical accuracy, the original dataset is

**Table 1.** Average (n = 3) concentrations obtained for ashed vegetation samples leached with de-ionized hot water. Abbreviations: DL, detection limit; RSD, relative standard deviation; wt, weight.

| Sample          | Sample wt | I (ppm) |      | Br (ppm) |      | F (ppm) |      | Cl (ppm) |      |
|-----------------|-----------|---------|------|----------|------|---------|------|----------|------|
|                 |           | mean    | %RSD | mean     | %RSD | mean    | %RSD | mean     | %RSD |
| Detection limit |           | 0.002   |      | 0.02     |      | 0.05    |      | 0.1      |      |
| VEG-V4a         | 0.25 g    | 3.85    | 8.1  | 67.37    | 4.8  | <DL     | <DL  | 7043     | 1.85 |
| VEG-V4a         | 0.50 g    | 3.99    | 6    | 73.5     | 1.3  | 14.45   | 1    | 6817     | 0.61 |
| VEG-V8a         | 0.25 g    | 0.099   | 4.8  | 66.3     | 1.1  | <DL     | <DL  | 4700     | 4.99 |
| VEG-V8a         | 0.50 g    | 0.108   | 2.8  | 70.7     | 1.1  | 9.76    | 3.7  | 4390     | 0.79 |

therefore considered sound for the purpose of examining element-distribution patterns; however, the linear trend of Au values identified in the original dataset (sequential samples) was determined an analytical artifact and those values have therefore been replaced by the new (lower) values to eliminate the false anomaly (a few other samples with elevated Au values in the northwestern part of the sample grid returned slightly lower values on repeat analysis, but very similar relative concentrations).

## Halogen Results

### Data Quality

Experimentation was undertaken to refine the analytical methodology for the four halogens; details of the methodology are described above.

The reproducibility achieved for field duplicate pairs is summarized in Table 2 and shows that, on average, the relative standard deviation for each of the halogens is about 20%, which is a reasonable level for reconnaissance samples.

Two vegetation ash samples were inserted by ALS as controls (VEG-V8a in Table 3 and Figure 4 and VEG-V4a in Table 4 and Figure 5) as well as control blanks and soil control OREAS-25a. The precision on all these controls was very good and somewhat better than that on the blind control (CDV-1a in Table 5 and Figure 6) because the latter

**Table 2.** Halogen relative standard deviations (RSD) for 20 field duplicate pairs.

| Average %RSD (n = 20 pairs) |       |       |       |       |
|-----------------------------|-------|-------|-------|-------|
| Analyte                     | Br    | Cl    | F     | I     |
| Average RSD                 | 19.8% | 20.3% | 16.8% | 17.9% |

**Table 3.** Halogen averages, standard deviations (Std dev.) and relative standard deviations (RSD) for control vegetation ash sample VEG-V8a.

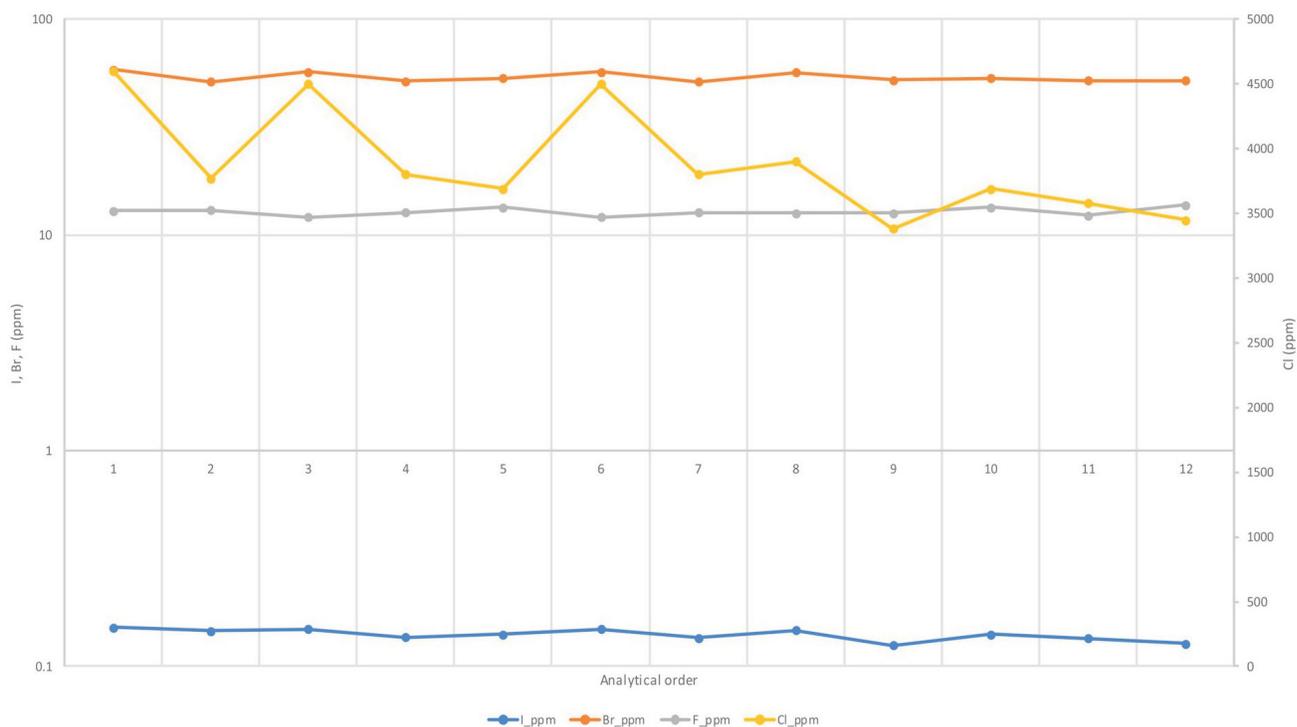
| Control VEG-V8a (n = 12) |      |       |       |      |
|--------------------------|------|-------|-------|------|
| Average (ppm)            | 0.14 | 53.87 | 12.77 | 3888 |
| Std dev.                 | 0.01 | 2.65  | 0.53  | 417  |
| %RSD                     | 6.1  | 4.9   | 4.2   | 10.7 |

**Table 4.** Halogen averages, standard deviations (Std dev.) and relative standard deviations (RSD) for control vegetation ash sample

| Control VEG-V4a (n = 5) |      |      |      |      |
|-------------------------|------|------|------|------|
| Average (ppm)           | 4.3  | 57   | 17   | 5838 |
| Std dev.                | 0.15 | 3.17 | 0.72 | 665  |
| %RSD                    | 3.5  | 5.6  | 4.2  | 11.4 |

**Table 5.** Halogen averages, standard deviations (Std dev.) and relative standard deviations (RSD) for blind control vegetation ash sample CDV-1a.

| Control CDV-1a (n = 24) |      |       |      |     |
|-------------------------|------|-------|------|-----|
| Average (ppm)           | 0.11 | 94.48 | 8.14 | 395 |
| Std dev.                | 0.01 | 3.57  | 5.91 | 23  |
| %RSD                    | 9.2  | 3.8   | 72.7 | 5.7 |



**Figure 4.** Chart of data summarized in Table 3 for control vegetation ash sample VEG-V8a.

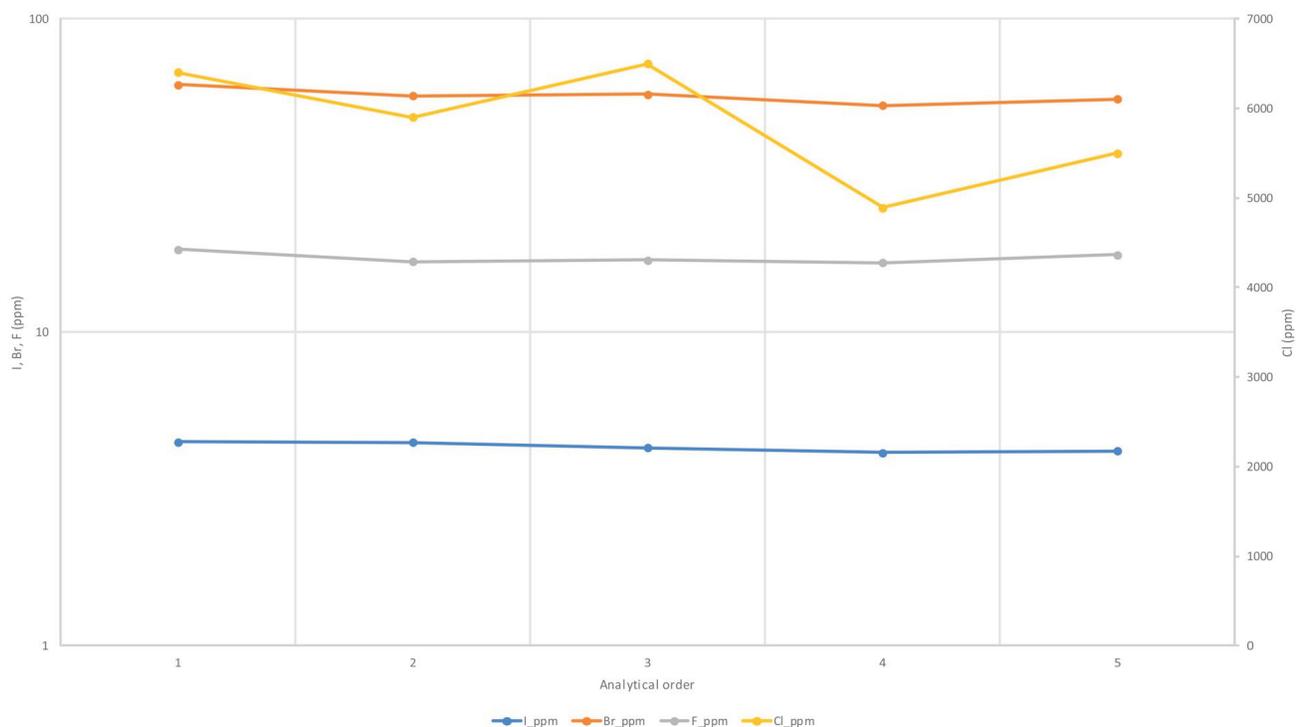


Figure 5. Chart of data summarized in Table 4 for control vegetation ash sample VEG-V4a.

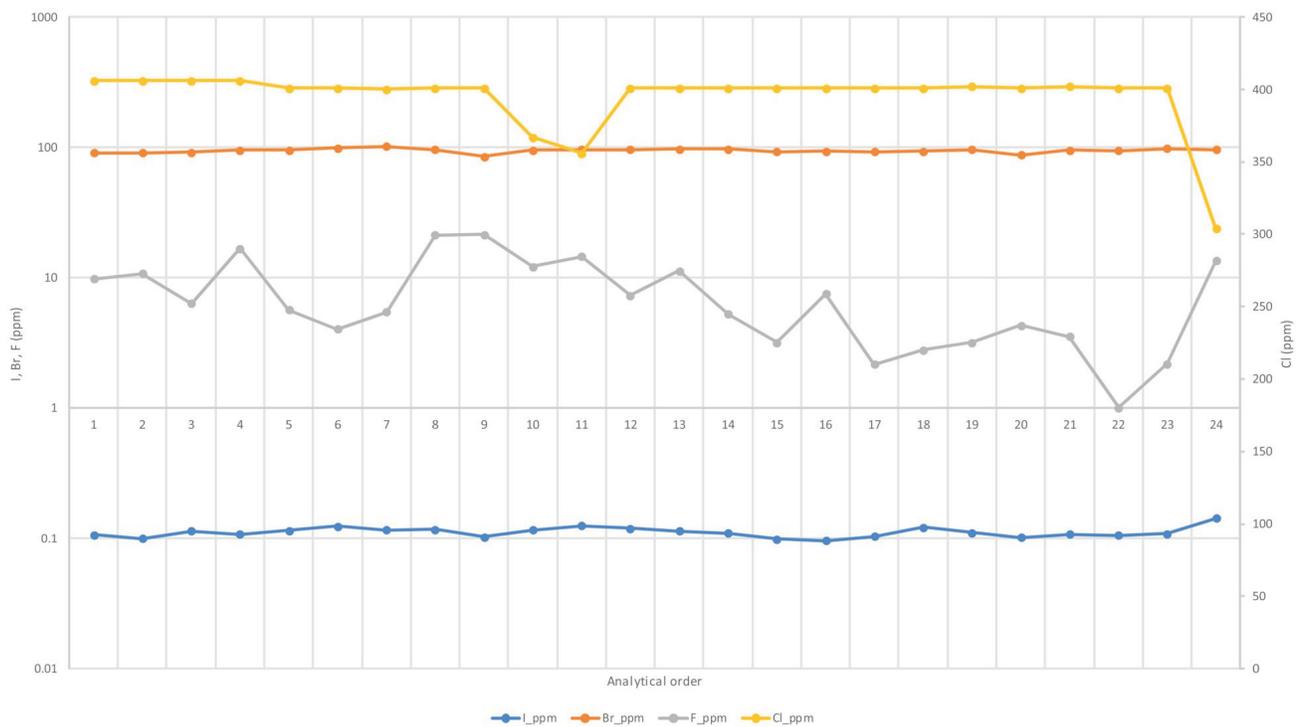


Figure 6. Chart of data summarized in Table 5 for blind control vegetation ash sample CDV-1a.

proved to have, in particular, lower concentrations of F than either the survey samples or laboratory controls.

### Survey Results

A preliminary plot of F concentrations (levelled to dry weight) is shown in Figure 7. Several areas of relative enrichment are apparent, notably the pronounced southwest trend in the northern half of the survey area. This trend follows the northern edge of the Chilcotin Group and coincides with a linear chain of lakes and an aeromagnetic break, suggesting that it could be reflecting a major structure. The other anomalies south of the trend all lie within Chilcotin Group basalts and could either indicate eruptive centres for the basalts or, more intriguingly, potential hydrothermal alteration in the underlying units exposed in windows through the basalt cover.

The relationships of these anomalous zones will be compared to new plots that will be prepared from the multi-element data provided by Jackaman and Sacco (2016), and with existing geophysical and Quaternary maps.

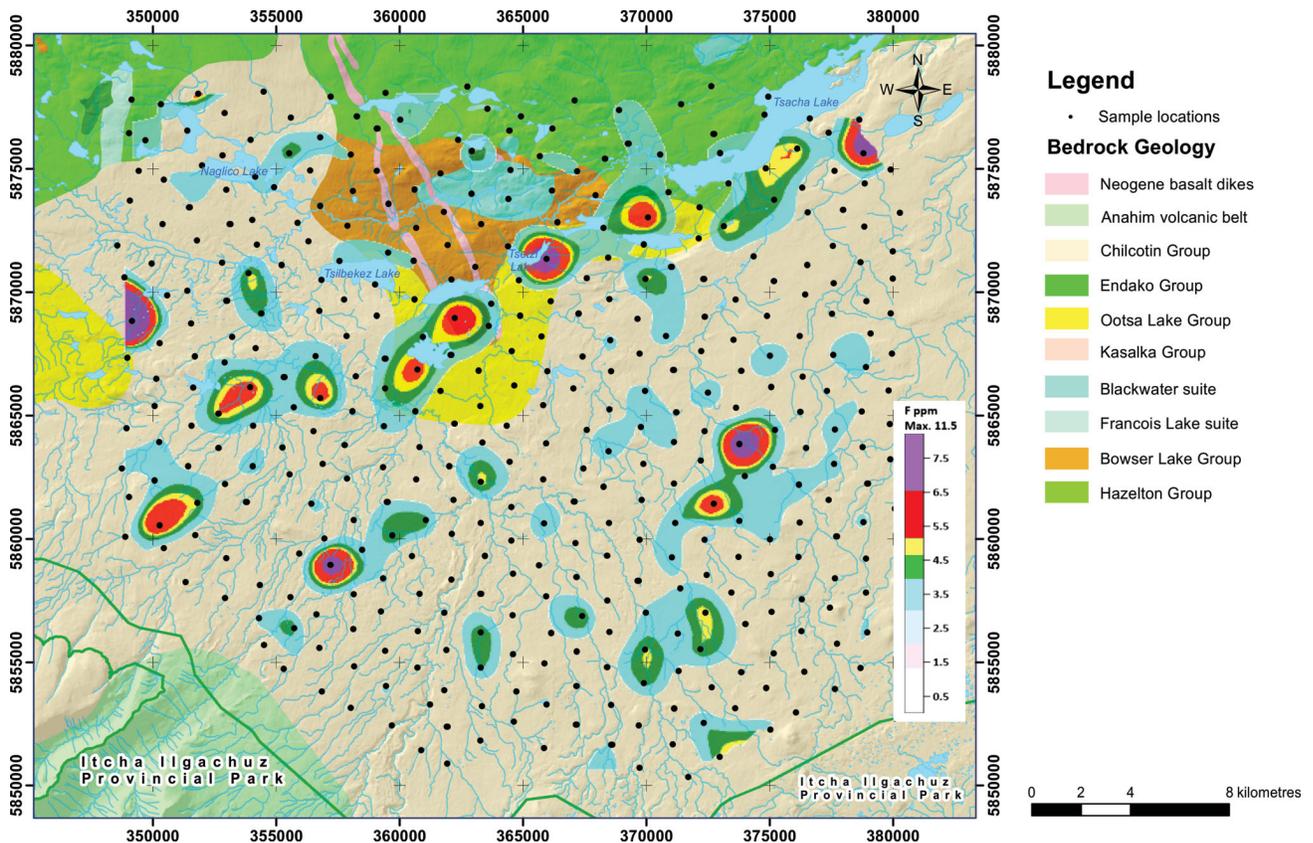
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**Figure 7.** Fluorine in spruce-treetop needles from central British Columbia, based on concentrations in ash levelled to dry-weight basis. Geological units after Angen et al. (2017).

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