



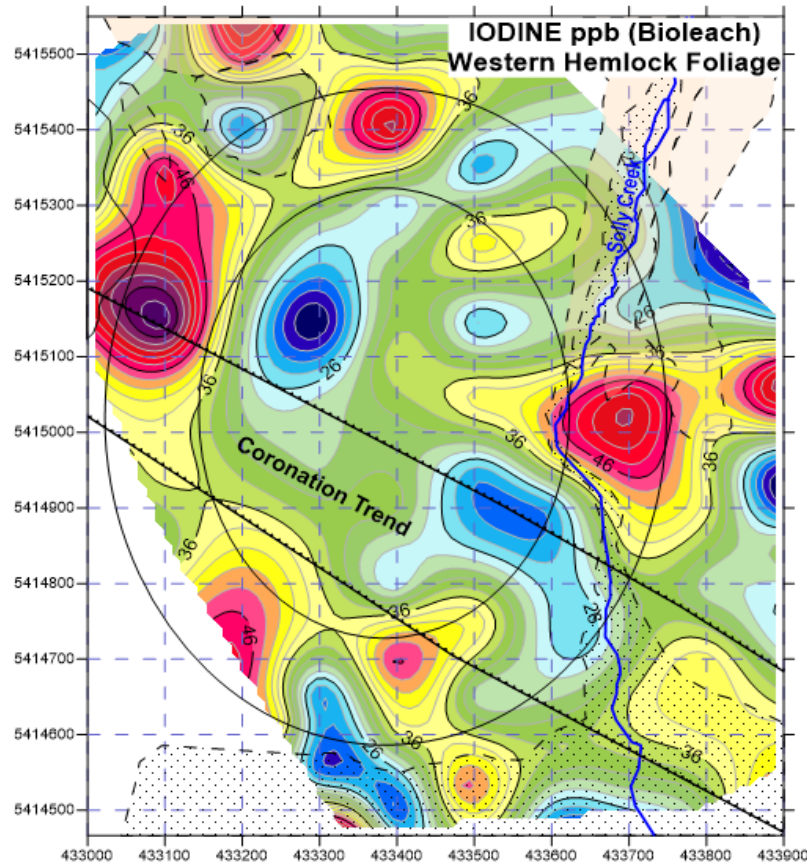
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Halogens and Other Volatile Compounds in Surface Sample Media as Indicators of Mineralization. Part 1: Lara VMS Deposit, Vancouver Island, BC (NTS 092B13)

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Executive Summary

The halogens (F, Cl, Br and I) are commonly associated with the emplacement of mineral deposits. Studies have found, too, that certain volatile compounds (e.g. ammonium) can also be enriched in surface media overlying buried deposits. Each element or volatile compound tends to have a different expression retained in the overlying soils and vegetation and, given that so much of British Columbia's mineral wealth is concealed by forests, Quaternary deposits and/or volcanic rocks, elucidation of these relationships could assist in mineral exploration programs. Of critical importance is to first develop rapid and economical analytical methods for precisely determining the concentrations of these volatile components in a variety of easily obtained surface media over disparate types of mineral deposit. Attempts to develop these methods have been outlined in two previous Geoscience BC studies (Dunn et al., 2007; Bissig et al., 2013) and the present study continues in refining analytical methods and defining signatures of volatiles in some previously un-reported sample media over two types of mineralization on Vancouver Island – volcanogenic massive sulphides (VMS - Lara) and an epithermal Au-Ag-Cu deposit (Mt. Washington). The latter study concentrates more on processes (Heberlein et al., 2017b), but includes several similar media to those reported here.

Such studies seek to determine the labile portions of volatile elements/compounds that may have emanated from a concealed mineral deposit, rather than their total contents in bedrock. Consequently, surface signatures tend to vary by both sample digestion method (e.g. partial leach) and sample medium. As a result, an anomalous response by one partial leach method, or in a particular sample medium, may differ in intensity and even location (e.g. distance from concealed mineralization) according to which volatile is being measured in which medium and by which method. Clearly, the complexity of signatures can be significant. The present study presents a step toward an understanding of the methodologies, processes and results that are obtained by a selection of analytical techniques and sample media.

At the Lara VMS deposit soils from the Ah and B horizons, and samples of the dominant tree species (Douglas-fir, western hemlock and western redcedar) were collected from 89 stations arranged in a 100 m spaced offset grid. Approximately every fifth sample station was designated as a multimedia site where additional understory species, including swordfern, Oregon grape and salal, were collected to provide background information on different species.

The warm water leach of Ah and B horizon soils and milled vegetation was defined earlier by G. Hall (in Dunn et al., 2007) as that which provided the optimal results for Br, Cl and I, when the instrumental finish was by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Fluorine required analysis on the same solution by ion selective electrode (ISE); however, element concentrations in vegetation were commonly at or below the detection limit of the method and consequently analytical precision was sometimes quite poor. In the present study, this leach was a primary digestion for many of the subsequent instrumental determinations, with initial emphasis on the use of a High-Performance Liquid Chromatography (HPLC) pump outfitted with a Metrohm ion suppressor and detection by conductivity (for Cl^- , PO_4^{3-} and SO_4^{2-}) and UV (for Br^- , NO_3^- , NO_2^- and I^-). An Auto Analyzer (automated analyzer using continuous flow analysis (CFA)), was used for determinations of nitrate (NO_3^-) and ammonium (NH_4^+). Fluorine determinations were initially by ion selective electrode (ISE). These methods met with mixed results, such that few compounds returned consistent

concentrations with adequate analytical precision. Ammonium results were sufficiently consistent to warrant plotting.

Prepared samples of Ah soils and western hemlock foliage were sent to Activation Laboratories for analysis by their proprietary weak leach method 'Bioleach'. Considerable research on methods for determining the halogens was undertaken at the laboratories of the BC Ministry of Environment (Victoria) and at ALS Minerals Ltd. (North Vancouver). Results are summarized in this report.

Key observations are:

1. Ammonium in dry western hemlock needles ('foliage' - WHF) exhibits a diffuse pattern of moderate enrichment surrounding the Coronation trend (the main area of known mineralization). A negative anomaly appears in the middle of the survey area where there is multi-element enrichment of a suite of commodity and pathfinder elements in Ah soils (e.g. Mo, Cu, Zn, Cd, Cs, Se, Tl, Hg, U and traces of Au and As).
2. B horizon soils digested in warm water yield strong Br and I anomalies in the above mentioned multi-element anomaly. The Cl pattern is more diffuse, and F enrichments are peripheral to the Br and I suggesting a possible outward zonation.
3. Bioleach of Ah horizon soil shows a strong I and Br anomaly in the same central area as the above suite of element enrichments and coincident anomalies of the alkali metals Cs and Rb (perhaps reflecting K metasomatism).
4. WHF samples do not delineate the central area mentioned above, but I defines a diffuse annular ring of anomalies 200-300 m distant (see frontispiece). This ring is indistinct for Br.
5. Of the miscellaneous species/tissues analyzed for halogens, swordfern have much higher F concentrations than other species. Highest ammonium levels are in swordfern and Oregon grape. Very high concentrations of Cl (>2% in ash) are present in the swordfern and salal foliage, with moderately high levels (0.6%) in western redcedar foliage.

Problems persist in obtaining stable halogen data in organic rich media by a low-cost method that can provide data for all the halogens at the low concentrations typically present. Ashing of samples prior to analysis goes a long way to circumventing these problems. The same problems apply to obtaining data for a range of other volatile compounds, with only ammonium generating adequate precision in the western hemlock foliage (WHF). Continuing research is required to refine the methodology, especially for F, and further testing over different types of mineralization is required to firmly establish the value of using halogens in an exploration program. The second component of this study investigates some of these questions and the processes that give rise to anomalous concentrations in surface media (Heberlein et al., 2017b).

Introduction

General Comments

The halogens (F, Cl, Br and I) are common constituents of igneous, metamorphic and sedimentary rocks (Billings and Williams, 1967). They 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. High halogen concentrations are also documented in high salinity liquid phases or in tiny secondary mineral phases in fluid inclusions in igneous and hydrothermal minerals (Kendrick et al., 2012; Kendrick and Burnard, 2013). In the hydrothermal environment halogens can be concentrated in alteration minerals such as micas, clays and topaz, and the gangue mineral fluorite. On exposure to surface conditions, these minerals weather and release their halogens as volatile gases (Br and I) and/or their more stable compounds, or water-soluble ions (F and Cl) that disperse to form detectable anomalies in the surficial environment (Trofimov and Rychkov, 2004).

In mineral exploration, there are case histories that demonstrate positive responses of all these elements and other compounds (e.g. NH_4 , SO_4 , PO_4) to zones of concealed mineralization (Al Ajely et al., 1985; Kydd, 1986; Ridgway, 1989, 1991; Ridgway et al., 1990; Trofimov and Rychkov, 2004). However, these methods have seen little or no application to the exploration for minerals in the extensively-covered terrains of British Columbia.

Previous Studies in BC

In 2005, Geoscience BC sponsored a project entitled “Halogens in Surface Exploration Geochemistry: Evaluation and Development of Methods for Detecting Buried Mineral Deposits” (Dunn et al., 2007). This initial study investigated the optimal analytical procedures available at the time for determining halogen concentrations in soil and vegetation, and provided new halogen data from the Mount Polley, QR and 3Ts deposits. A recommendation from this study was that since a clear response of labile halogens in soils and vegetation to known mineralization had been established, targets concealed by overburden (both Quaternary and volcanic) needed to be tested and analytical methodology needed to be refined. Numerous analytical problems were identified, and it was concluded that further analytical research was required to better define the methods required for obtaining improved analytical precision and accuracy at the low levels of halogen elements typically present in a water leach of soils and vegetation, and at the costs acceptable to mineral exploration.

A second finding was that halogen signatures vary according to the nature of the mineralization: whereas I may provide the best signature in one area, F may be best in another. This indicates that each style of mineralization is likely to generate a different suite of positive halogen responses that have yet to be clearly defined; hence analysis for all four halogens is advisable.

Bissig et al. (2013) as part of a wider study looking at geochemical responses of blind Cu-Au porphyry-style mineralization beneath Chilcotin basalt cover at Woodjam (near the community of Horsefly, central B.C.), demonstrated that the partial extraction techniques Bioleach and Enzyme Leach produced robust responses in Br and I anomalies over blind mineralization at the Three Firs prospect.

The current project expands on the 2005 and 2013 studies. It further investigates halogen and other volatile compound responses (not included in the 2005 study) in organic media over blind and thinly covered mineralization. Two study sites, both on Vancouver Island, were selected for this investigation: Lara is a VMS target (a commodity for which the halogen response has not previously been tested in B.C.) that is buried by 5 to 10 metres of till; Mount Washington is an epithermal Au-Ag-Cu system with a thin veneer of overburden. This report summarizes the field program and objectives of the first of these – Lara. A second report outlines the approach at Mt. Washington (Heberlein et al., 2017b). Because of budgetary constraints, the Lara study investigated the use of fewer techniques, but a similar range of volatile compounds than those applied at Mt. Washington. Objectives of the two studies were to expand the range of sample media tested and to investigate the effectiveness of commercially available analytical methods and new instrumentation (some not available in 2005) for detecting mineralization-related halogen and volatile compound responses.

The Lara investigation tests the geochemical responses of halogens and other mineralization-related compounds (e.g. NH_4 , PO_4 and SO_4) in a variety of organic media, including: Ah horizon and B horizon soils, foliage and bark from the most prevalent tree species, and foliage from selected understory species. Volatile element distributions are compared with selected commodity and pathfinder element signatures for the same media.

Relevance to the Exploration Community

This study is designed to provide the mineral exploration community with an understanding of the potential advantages of determining volatile components, derived from zones of VMS and epithermal Au mineralization, which accumulate in soils, common conifer trees, and in shrubs in regions of contrasting cover environments. The Mt. Washington study focuses more on processes and the analysis of several alternative sample media (Heberlein et al., 2017b). These studies examine the relative capabilities of each medium for preserving the secondary geochemical dispersion patterns related to mineralization, and assess the value to the exploration community of an alternative analytical approach for geochemical sampling programs in areas where conventional soil-sampling methods are found to be ineffective or of limited use and/or where contamination from mining activities might complicate the use of other sampling media.

Study Area

The test site at the Lara VMS deposit (Coronation trend), located near Chemainus, is readily accessible by a good road network minimizing the logistical costs required for the field component of the study (Fig. 1).

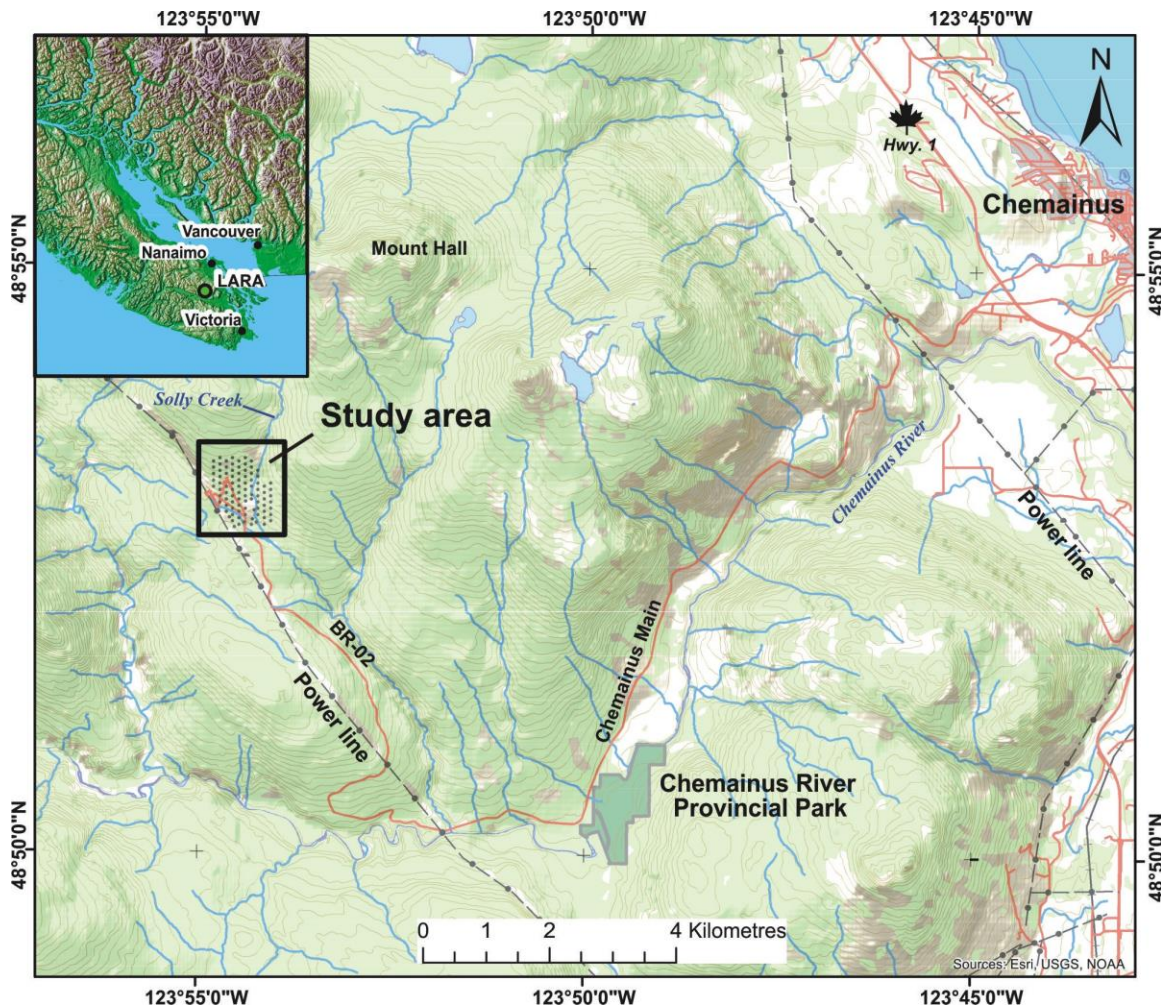


Figure 1: Location of the Lara study area, east-central Vancouver Island, showing sample stations. Contains information licensed under the Open Government License – Canada.

Location Access and Topography

The Lara deposit ('Lara') is in the Victoria Mining Division of southern Vancouver Island, 75 km north of Victoria, 15 km northwest of Duncan and 25 km west-southwest of Chemainus, which was the logistical base for the field portion of the study. Access to the project area is via the active Chemainus main logging road to kilometre 19 and then the Br 02 Mt. Brenton Forest Service Road to kilometre 7.5. From there, a network of secondary logging roads, drilling roads and a BC Hydro right of way provide access to the sampling area.

Lara is located at the boundary between the Vancouver Island Ranges to the north and west, and the Nanaimo Lowlands to the south and east (Holland, 1976) in an area of rolling topography. The study site lies on the lower southern slopes of Coronation Mountain (to the northwest) and Mount Hall (to the northeast) between elevations of 610 and 770 m (Fig. 2). Solly creek is the main drainage separating the two peaks. It crosses the study area from north to south before turning southeastwards to drain into the Chemainus River.

Surficial Geology

There are no published surficial geology maps for the immediate Lara area; only the area to the east where a general ice-flow direction is interpreted to be mostly from a northerly direction (Blythe and Rutter, 1993). The distribution of surficial materials shown in Figure 2 has been interpreted primarily from field observations and aerial photographs. Regolith and geological mapping undertaken by Matt Bodnar for his M.Sc. thesis at the Mineral Deposits Research Unit (MDRU – University of British Columbia) are incorporated into this interpretation.

Most of the project area has a veneer or blanket of glacial till (dark green; Fig. 2). This is interpreted to be a basal or lodgement till; it is exposed in road cuts, stream banks, trenches and a large open cut near the Coronation zone portal. While difficult to estimate its thickness from present day exposures, drilling and trenching records show that it varies from <1 m to >50 m (Kapusta, 1990; Archibald, 1999). The presence of outcrops and bedrock-derived colluvium within the till-covered area (pinks and browns; Fig. 2) suggest that there is well-developed buried bedrock topography. In general, there is a gradual thinning of the till deposits up-slope.

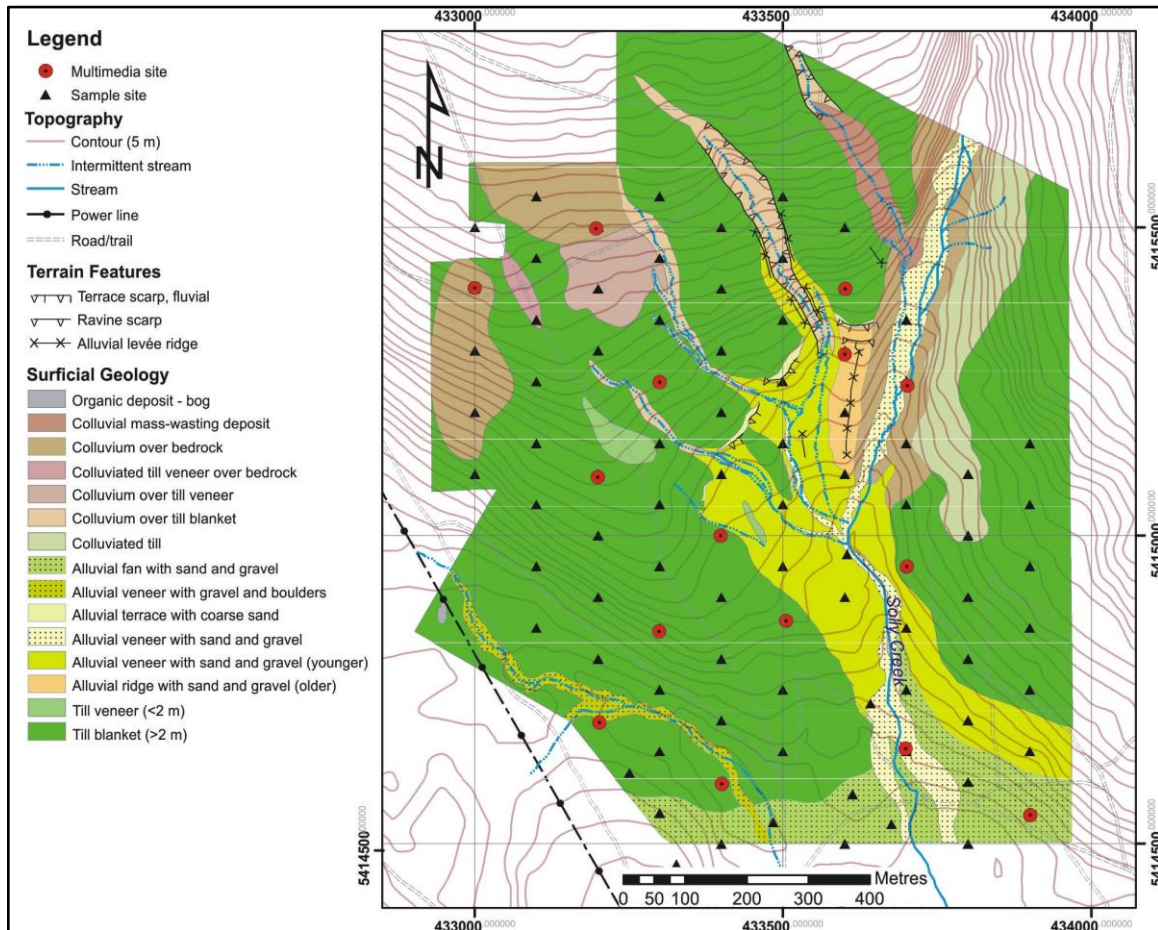


Figure 2: Surficial geology of the Lara study area, east-central Vancouver Island, showing sample stations. Contains information licensed under the Open Government License – Canada.

Recent mapping by Bodnar (pers. comm., 2016) has augmented the interpretation of the surficial geology in the central part of the survey area. Alluvial deposits consisting of coarse sands, gravels and channel conglomerates (pale green; Figure 2), define a paleochannel system that is now occupied by Solly creek. First order tributaries show evidence of erosional recession to the northwest with back scarps incised into and causing reworking of the till blanket. A recent land slide occurring in the northern-most tributary on Figure 2 has delivered large amounts of unsorted sediment into Solly creek. The apparently rapid incision of the drainage system has caused it to dissect its own alluvial deposits. Remnants of older alluvial terraces occur along the hillside to the west of Solly creek between elevations of 660 and 675 m (pale yellow stipple; Fig. 2). These deposits define the upper edge of a 200 m-wide alluvial sand and gravel plain bordering the present-day creek and extending down to the base of slope where it spreads out into what appears to be an alluvial fan (pale green stipple; Figure 2). A remnant of an even older alluvial ridge or terrace (orange; Fig. 2) is preserved as an interfluvium on the west side of Solly creek.

Alluvium related to the active drainages is shown by yellow stippled patterns in Figure 2. Solly creek is the main drainage in the study area. Its upper reaches (above 650 m) are constrained by a steep-sided canyon that has incised through the till and into the underlying bedrock. Upper slopes on the east side of the canyon are covered with colluviated till deposits (pale brown; Fig. 2). The steeper lower slopes adjacent to the creek are made up of bedrock-derived colluvium veneer overlying bedrock (dusky pink; Fig. 2). Bedrock exposures (too small to be visible at the scale of Fig. 2) can be found along the eastern canyon wall as well as in the stream bed itself. Similar colluvial deposits and outcrops are present on the west side of the canyon, but these are capped by unmodified till and the older alluvial gravel ridge mentioned above.

A shallow colluvial veneer over bedrock is also present at the northwestern limits of the study area (medium brown; Fig. 2). Two separate areas are mapped but they could be part of a larger area of bedrock-derived colluvium extending up slope to the northwest. Downslope the colluvium forms a thin veneer over glacial till.

Soil profiles developed on the tills are eutric brunisols (Fig. 3). They include a surface LFH layer and an underlying thin Ah horizon lying on top of a generally undifferentiated brown Bm horizon. Iron enrichment at the top of the Bm horizon (Bfj horizon) is present at some localities particularly over alluvial and colluvial deposits. The presence of a discontinuous eluviated horizon (Aej) at some of these localities indicates incipient podsolization over better drained areas.



Figure 3: An example of an eluviated Eutric Brunisol soil profile. Photo courtesy of Matt Bodnar.

GEOLOGY

The geology of the Lara area is complex, and several different interpretations have been published. Most recently, a detailed synopsis and re-mapping of diamond drilling results has been undertaken as part of a M.Sc. thesis by Bodnar (pers. comm., 2017). His map is used as the underlay to the element plots presented in this report.

Lara is underlain by volcanic and volcanoclastic sedimentary units belonging to the McLaughlin Ridge Formation of the Sicker Group (Massey, 1992; Krocker, 2014). The Sicker Group (Mississippian-Pennsylvanian) is known as an important host for Kuroko-type VMS mineralization: the principal economic deposits being the H-W, Lynx, Myra and Price deposits from the Buttle Lake camp (Juras, 1987) located in the Buttle Lake uplift west of Courtenay. Lara lies in a separate uplift, the Cowichan-Horne Lake uplift, in the southern part of the island. VMS style mineralization is hosted by a west-northwest striking, northeast dipping package of volcanoclastic sediments consisting mostly of sandstones, siltstones, argillites and tuffites (Krocker, 2014). Volcanic rocks are volumetrically subordinate to the volcanoclastic sediments. They include aphyric and porphyritic (feldspar, pyroxene and hornblende) rocks, lapilli tuffs and breccias of intermediate to mafic composition that lie in the immediate hanging wall to the Coronation trend (Fig. 4). Felsic units are relatively common in the Lara area. A narrow quartz-phyric rhyolite crystal and an ash tuff package, known as the Southern Rhyolite sequence (Wells and Kapusta, 1989), hosts mineralization at the Coronation zone. The unit is intruded by several sill-like gabbro bodies. A footwall rhyolite, possibly a dome complex consisting of quartz and

feldspar-phyric rhyolite, has also been identified in a few drill holes penetrating the footwall of the Coronation zone. Throughout this report, the faulted block that occurs north of the Fulford fault is referred to as the Coronation trend – incorporating the Coronation and Hanging Wall zones.

South of the Coronation trend, the Sicker Group is abruptly truncated by the Fulford fault: a bedding sub-parallel reverse fault that thrusts Sicker Group over younger Nanaimo Group sedimentary units.

Lara mineralization occurs in seven discrete zones (Krocker, 2014). Three of these including the Coronation zone and the Hanging wall zone which together make up the Coronation trend, occur in the area covered by this study. The most important of these is the Coronation zone, which hosts massive, banded/laminated and stringer-style polymetallic sulphide mineralization. The position of these zones compiled from historical drilling results is shown in Figure 4 (Bodnar, pers. comm., 2016, 2017). The zones have been interpreted as separated by a series of thrust faults dipping steeply to the northeast thereby repeating the mineralized horizons. There are also numerous lesser zones, small showings, geochemical anomalies and geophysical targets that, despite the locally extensive cover, trace the mineralized stratigraphy back towards Mount Sicker.

Treasury Metals Inc., who hold the mineral claims, reports an indicated resource estimate (for a 1% Zn block cut off) of approximately 1,146,700 tonnes with an average grade of 3.01% Zn, 32.97 g/t Ag, 1.05% Cu, 0.58% Pb, and 1.97 g/t Au for the Coronation trend with an additional 669,600 tonnes, with an average grade of 2.26% Zn, 32.99 g/t Ag, 0.90% Cu, 0.44% Pb, 1.90 g/t Au of inferred resource (http://www.treasuremetals.com/s/lara_property.asp). The Coronation trend crosses the southern third of the study area.

Hydrothermal alteration, present mostly in the structural hanging wall east of the Coronation zone, consists of strong pervasive sericitization defined chemically by Na depletion, with K and Ba enrichment. It is associated with elevated Zn and Cu values, local silicification and disseminated pyrite (Peatfield and Walker, 1994; Wells and Kapusta, 1990a).

An ongoing MDRU geochemistry research project is investigating the processes and controls of labile element mobility, and aims to develop a process-based model of trace element dispersion in the surface environment above concealed massive sulphide mineralization: this work provides a context and back drop to that study.

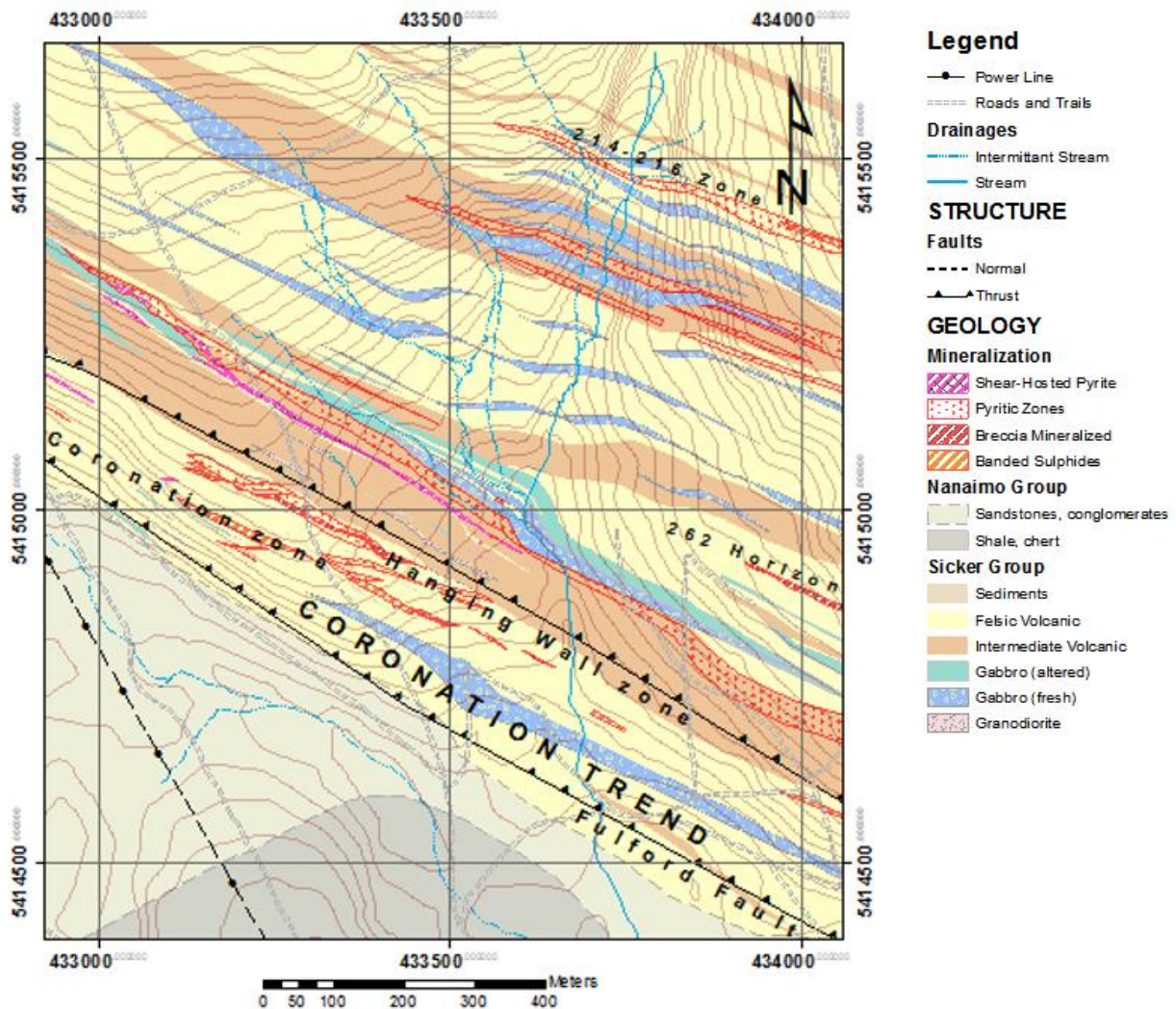


Figure 4: Geology of the Lara study area, east-central Vancouver Island, showing surface projections of the mineralized horizons (red hatching). Mapping after Bodnar (pers. comm., 2017).

Vegetation

The entire project area was logged in the 1950's. Consequently, the present-day vegetation consists of mixed second growth forest comprising mostly equal coverage of western redcedar (*Thuja plicata*), western hemlock (*Tsuga heterophylla*) and Douglas-fir (*Pseudotsuga menziesii*) – Figure 5.



Western hemlock (*Tsuga heterophylla*)



Western redcedar (*Thuja plicata*)



Douglas-fir (*Pseudotsuga menziesii*).

Figure 5: Common conifer trees at Lara

Other species present include western white pine (*Pinus monticola*), paper birch (*Betula papyrifera*) and red alder (*Alnus rubra*). Understory species (Fig. 6) vary considerably from place to place. Western swordfern (*Polystichum munitum*) is common in moist coniferous forests at low elevations. It grows best in a well-drained acidic soil of rich humus. Salal (*Gaultheria shallon*), a leathery-leaved shrub in the heather family, is tolerant of both sunny and shady conditions at low to moderate elevations. It is a common coniferous forest understory species in coastal areas of British Columbia and the northwest USA, and may dominate large areas and form dense, nearly impenetrable thickets on southwest facing slopes. Oregon grape (*Mahonia aquifolium*) has holly-like leaves and prefers the more canopied areas – Fig. 6).



Salal (*Gaultheria shallon*)



Oregon grape (*Mahonia aquifolium*)



Western swordfern (*Polystichum munitum*)

Figure 6: Common understory species at Lara.

Sampling

The primary aim of the sampling program was to collect a selection of organic media to test for halogens and other mineralization-related compounds (including NH_4 , SO_4 and PO_4).

B horizon soils for pH Measurements and Halogen Determinations

Samples for soil pH and electrical conductivity measurements were collected at each sample site (Fig. 7). Approximately 50 g of material was collected from the top centimetre of the B horizon. Care was taken to avoid organic-rich material from the overlying Ah horizon as organic acids may interfere with or mask the sought-after bedrock responses. Samples were placed in Kraft paper soil sample bags.

Ah horizon soils

Ah horizon soil sampling involved rolling back the surface moss-mat and leaf-litter layer (LF and LFH horizon) and scraping the black humic material accumulated on top of the mineral soil profile. To obtain enough material (50–75 g) and to create a composite sample to reduce within-site variability, several patches were sampled at each station and put in Kraft paper sample bags.

Vegetation

Considerably more samples were collected than the scope of the project could afford to be analyzed. However, sampling is quick and easy and it was unknown which medium might provide the most informative response to the concealed mineralization, so emphasis was placed on collecting several of the most common species at all sample stations. Samples not analyzed initially would be available for detailed analysis once baseline data were established or for future investigations.

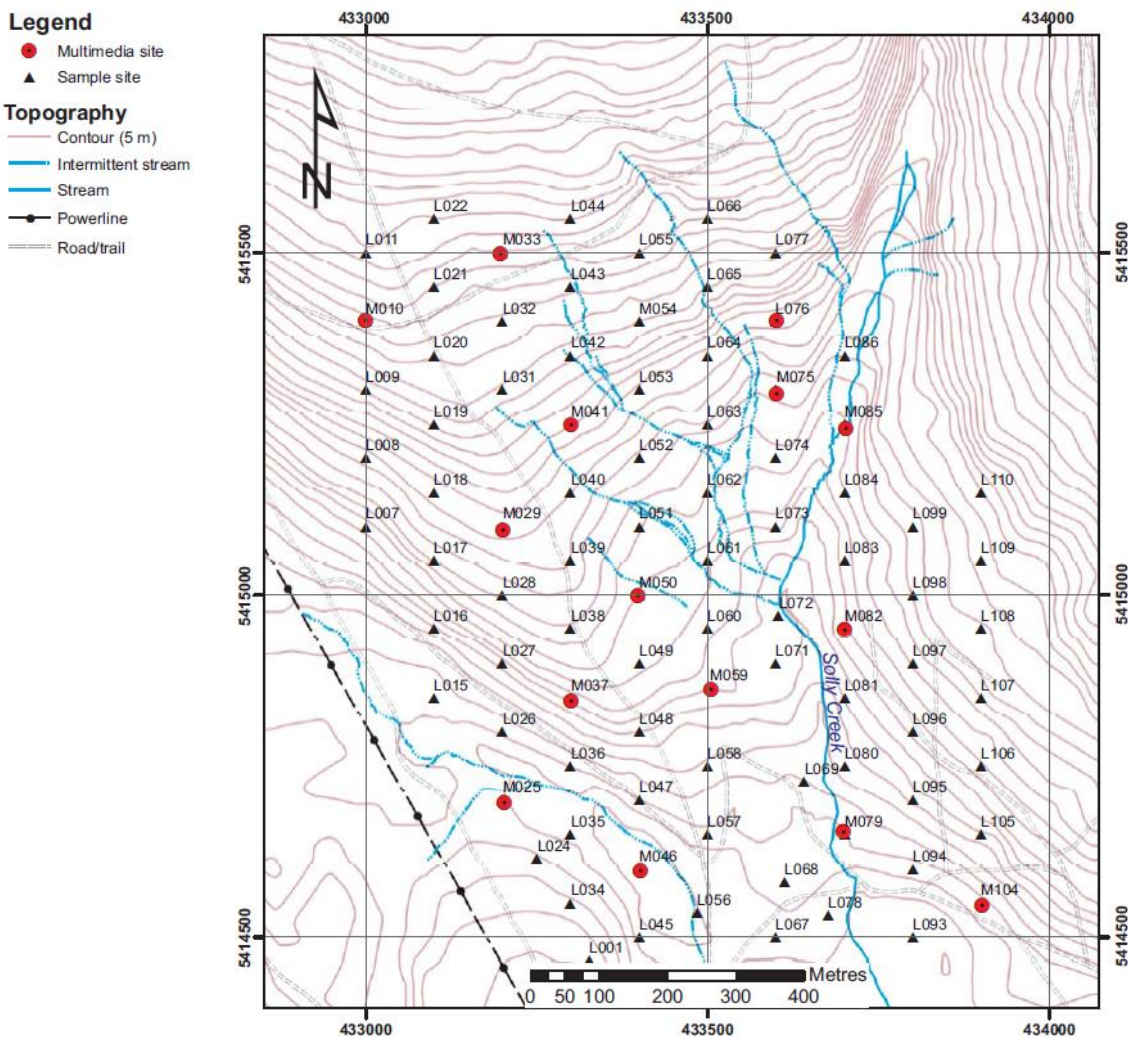


Figure 7: Lara sample location map.

Samples of the dominant tree species (Douglas-fir, western hemlock and western redcedar) were collected from a maximum of 89 stations arranged in a 100 m spaced offset grid (Fig. 7).

Approximately every fifth sample was designated as a multimedia site where additional understory species, including swordfern, Oregon grape and salal, were collected to provide background information on different species. Numbers and types of samples collected (but not all analyzed) are summarized in Table 1 and their locations shown in Figure 7. Limitations on the availability of sample media at some sample stations meant that not all media could be collected at all the desired sites. This was especially true in areas of ground disturbance caused by road building, mining and drilling activities as well as in swamps and major drainages. Detailed lists of all samples and field observations are shown in Appendix 1, Table A1.

Table 1: Numbers and types of samples collected at Lara.

Sample medium	No. Samples
Western hemlock foliage (WHF)	89
Western hemlock bark (WHB)	67
Western redcedar foliage (RCF)	88
Douglas-fir bark (DFB)	79
Salal foliage (SALF)	17
Swordfern foliage (SF)	8
Oregon grape foliage (OGF)	8
Ah horizon soil	89
B horizon soil	81

Twigs and foliage comprising the most recent 5-7 years of growth were collected from both western hemlock and western redcedar. Samples comprised 5-7 lengths of about 25 cm snipped from around the circumference of a single tree. Samples of outer bark from Douglas-fir and western hemlock were obtained by scraping the scales from around the circumference of neighbouring trees, using a hardened steel paint scraper, and the scales put into a standard 'Kraft' paper soil bag (about 50 g – a fairly full bag).

Foliage from the understory species collected at the multi-media sites (Fig. 7) was sampled by gripping a stem near the base and pulling upwards to strip off the leaves. Leaves were collected from two or three plants and placed in a 12.5 by 7 inch (32 x 18 cm) Hubco New Sentry II[®] fabric sample bags.

Analytical Methods

General

Whereas the scientific literature contains many papers dealing with the analysis of volatile elements, most of these methods are time-consuming and therefore expensive to the point that they are beyond the scope of most exploration budgets, therefore are not offered by most commercial laboratories. For example, Villa (1979) describes a method for fluoride that requires stirring dried vegetation with 0.1 N perchloric acid for 20 minutes and then following a standard addition procedure with wait periods between each phase. Such a method would be too expensive to be practical for an exploration program. The objectives of the present study are to

develop procedures that are rapid, cost-effective and which provide data for a range of volatile components using commercially available analytical instrumentation.

Currently, most commercial laboratories offer F analysis of inorganic samples by Ion Selective Electrode (ISE) after either a KOH or Na₂O₂ fusion. While appropriate for determination of F and Cl in some types of inorganic samples, the ISE method has many potential interferences and detection limits that are too high (typically around 20 ppm for KOH fusion and 0.01% for Na₂O₂ fusion) to be of use for the detection of subtle secondary dispersion patterns.

Ion chromatography (IC) has lower detection limit capabilities for the analysis of F, Cl, Br and I, but for water leached or nitric acid-digested surficial samples it is compromised by interferences with nitrate ions and organic compounds. Chlorine can typically be detected down to 0.001% by XRF on a lithium borate fusion and to 50 ppm by IC on a KOH fusion; detection limits that are again too high to be of practical use for surficial exploration sample media. Pyrohydrolysis coupled to IC is the standard for F and Cl determinations on samples with significant organic content, but it is an expensive method that is not widely available outside coal-focused laboratories (Hall et al., 1986).

Lower detection limits in the order of 0.5 ppm can be achieved for Cl, Br and I by instrumental neutron activation analysis (INAA). By ICP-MS the lower limits are pushed down even further to <0.01 ppm for Br and I, which is low enough to reveal geological background in most surface media. Actlabs publish detection limits of 5 ppb for Br and 1 ppb for I for their proprietary Bioleach method (used in this study). ALS achieves detection limits of 0.02 ppm for Br and 0.002 ppm for I on their water leach-ICP-MS method.

Soil pH and electrical conductivity measurements

Soil pH measurements were made on 1:1 slurries of soil and distilled water using the method described by Heberlein and Samson, 2010. Approximately 20 mL of soil was placed in a graduated plastic beaker and the volume was brought up to 40 mL with distilled water. The mixture was thoroughly stirred. Readings were taken on the slurry after 20 seconds using an Oakton Industries pH Testr 30 portable pH meter. A second reading was taken in the same manner after the addition of one drop of 5% acetic acid. The meter was soaked in tap water overnight prior to taking the readings. A three-point calibration was made before the pH readings with pH 4.01, 7.0 and 10.1 NIST pH buffer solutions; pH values were converted to H⁺ ion activities for plotting.

The acidified pH (pHa) is an indication of the buffering capacity of the soils and the closer the pHa values are to the original pH, the greater the buffering capacity. Readings were recorded into an Excel spreadsheet and converted to H⁺ concentrations and the inverse-difference hydrogen ions, or IDH, calculated for interpretation (Smee, 2009). IDH is the inverse of the difference between acidified and non-acidified H⁺ concentrations in the soil and is a measure of the soil buffering capacity. It is thought to be sensitive to remobilized carbonate around the edges of reduced columns (Hamilton, 1998; Smee, 2009).

Sample preparation

Vegetation and soil samples were oven-dried at 80° C for 24 hours to remove all moisture. Ah and B horizon soil samples were sieved to -80 mesh (177 microns) in preparation for analysis of the finer fraction. Foliage was separated from twigs. All foliage and bark samples were then

reduced to a fine powder in a coffee mill. In general, particles were finer than about 0.5 mm, but particle size is not important for obtaining consistent results (Dunn, 2007).

Table 2: Summary of analytical methods used for Lara samples.

Sample Media	Laboratory	Digestion	Analytical methods
Ah horizon – All sites	ALS Minerals, N. Vancouver, BC	Aqua regia	ME-MS41L
Ah horizon – All sites	ALS Minerals, N. Vancouver, BC	Warm water leach	ME-MS14L including all halogens
Ah horizon – All sites	ALS Minerals, N. Vancouver, BC	Ash at 485°C and warm H ₂ O	Halogens - ME-HAL01a ²
Ah horizon – All sites	Actlabs, Ancaster, ON	Bioleach	ICP-MS
B horizon - All sites	ALS Minerals, N. Vancouver, BC	Ash at 485°C and warm H ₂ O	Halogens - ME-HAL01a ²
WHF – All sites	Actlabs, Ancaster, ON	Bioleach	ICP-MS
WHF – All sites	ALS Minerals, N. Vancouver, BC	Ash at 485°C and warm H ₂ O	Halogens - ME-HAL01a ²
WHF – All sites	BC MOE Laboratory ¹ , Victoria	Warm H ₂ O	HPLC-IC ³ for Cl, Br, I, PO ₄ and SO ₄ ; F by ISE ⁴
WHB, RCF, SAL, SF, OGF	BC MOE Laboratory ¹ , Victoria	Warm H ₂ O	ICP-MS
WHF, WHB, RCF, SAL, SF, OGF	BC MOE Laboratory ¹ , Victoria	Microwave HNO ₃	ICP-MS
WHB, RCF, SAL, SF, OGF	ALS Minerals, N. Vancouver, BC	Warm H ₂ O	ME-MS14L and ME-HAL01a ²

¹ - B.C. Ministry of Environment (Environmental Sustainability and Strategic Policy Division, Knowledge Management Branch) in Victoria, BC.

² - ICP-MS and IC

³ - High Performance Liquid Chromatography/Ion Chromatography (HPLC-IC).

⁴ - Ion Selective Electrode

High Performance Liquid Chromatography and Ion Chromatography (HPLC-IC)

Initially, a split of each sample of western hemlock needles (WHF) was subjected to a warm water leach in accord with the method developed by G. Hall under Geoscience BC Project 2005-008 (Dunn et al., 2007):

Soil and vegetation samples were leached by placing a 1 g sample in 10 mL deionized water which was then vortexed and allowed to sit for 1 hour at 30° C in an incubator. Samples were then centrifuged and filtered through a 0.45 micron filter.

Leachates from approximately 200 vegetation samples were analyzed by HPLC-IC for Cl, Br, I, PO₄ and SO₄ at the BC Ministry of Environment (Environmental Sustainability and Strategic Policy Division, Knowledge Management Branch – BCMOE) in Victoria, BC, under the direction of the laboratory manager, Clive Dawson. The same solutions were analyzed on an Auto Analyzer (an automated analyzer using continuous flow analysis (CFA)), for nitrate (NO₃) and ammonium (NH₄) and for F using an ion selective electrode (ISE). From the controls, it was evident that the first results showed there to be considerable variability in the analytical data such that extensive research was subsequently undertaken to refine the methodology. After several iterations of data, the final laboratory report summarized the extensive experimentation:

Finely ground vegetation samples were incubated at 30°C for 1 hour (2 g in 20 mL 18 mohm H₂O). These water extracts were then filtered using a 0.45µm nylon syringe filter, with some difficulty. In this case, a large batch of over 100 samples was extracted at once. Since temperature and time seem to be critical to achieving precise data over a large sample set, in the future (we) suggest smaller batches, horizontal shaking at room temperature, strict timing and immediate filtering.

This water leach was then analyzed using a Waters 1525 HPLC pump outfitted with a Metrohm ion suppressor and detection by conductivity (for Cl⁻, PO₄³⁻ and SO₄²⁻) and UV (for Br⁻, NO₃⁻, NO₂⁻ and I⁻). The analysis began using a Grace Novosep A-2 Anion

column (5µm, 250 x 4mm). These samples proved to be very hard on the column because of the large amounts of organic compounds also dissolved in the extract. Each run was for 45 minutes and 2 injections were required for each sample, to determine high levels of Cl^- , PO_4^{3-} and SO_4^{2-} and low levels of Br^- , NO_3^- , NO_2^- and I^- . The column's ability to resolve peaks degraded over time; therefore, a new column was used to finish the analysis (Shodex SI-524E, 5µm, 250 x 4mm). This column proved to have much better resolution than the previous one. But over time, with these harsh samples, degradation also occurred, so it is advised that the column be flushed and cleaned often while closely monitoring the peak resolution. These columns can be >\$1500, therefore the cost associated with this analysis is large if a column is ruined by these organic-rich samples.

Overall, the anion analysis by HPLC proved to be very difficult due to:

1. The high organic content of the water leaches; this added many unknown peaks to the chromatograms (which varied with sample type), making anion identification and quantification difficult.
2. This organic material is also hard on the column, so over time the resolution degraded. It was unclear at times (especially for Cl^- and PO_4^{3-}) if a single peak was actually the anion overlapping with unknown peaks or not, resulting in sometimes false/enhanced integrations, leading to poor precision over a large data set.
3. Initially, small batches of controls were tested for their viability using this ion chromatography analysis. The small batch analysis results and precision appeared to be good, but this was misleading. The quick degradation of the column affected the resolution and retention time of the peaks, therefore over large batches of samples (taking days or weeks to run) the precision dramatically decreased, and was mainly due to peak overlap.
4. Br^- , NO_3^- , NO_2^- and I^- were at such low concentrations that the peaks were almost indistinguishable from the bumpy baseline, making identification and quantification very difficult or impossible.
5. Over time the retention times of the anions shifted downwards, so rather than relying on just the retention time of each anion for identification, patterns in the chromatograms were also used to "identify" peaks. However, those identifications at such low concentrations for Br^- , NO_3^- , NO_2^- and I^- were somewhat doubtful.
6. F^- elutes at the beginning of the run, but it was too difficult to resolve and measure the peak using this HPLC setup. ISE can be used to measure F^- if the concentrations are >0.1ppm.
7. Duplicate samples run side by side did not always agree with each other. With everything being equal during the HPLC analysis, possibly the extraction method itself is not optimal. An incubation of 1 hour at 30°C is not much different than sitting on the bench top at room temperature. So, if large batches of samples are extracted, the time between the first and last sample being filtered could significantly change the results. Therefore, small batches and strict timing are critical if using incubation at 30°C.

Given the constraints and problems outlined above, the laboratory concluded that the detection limits were those shown in Table 3. However, the lack of precision was a significant problem and rendered many of the data unusable, as discussed below.

Table 3: Detection limits for HPLC anions after method optimization.

HPLC Analyte	Detection Limit (ppm)	Detection Method
Br ⁻	0.65	Ultra-violet
I ⁻	0.65	Ultra-violet
NO ₂ ⁻	0.40	Ultra-violet
NO ₃ ⁻	0.40	Ultra-violet
Cl ⁻	0.65	Conductivity
PO ₄ ³⁻	2	Conductivity
SO ₄ ²⁻	1	Conductivity

Halogen Analysis by Ion Chromatography (IC) and ICP-MS

The next phase of experimentation was carried out at the ALS geochemical laboratory in North Vancouver. ALS chose to analyse Br and I by ICP-MS, but testing for F and Cl required method development on the IC to remove or nullify the nitrate (NO₃) and organic compound interferences common in the analysis of surficial materials. Three different methods were tested:

- 1) Addition of ultrapure nitric acid to a warm water leach to oxidize organics. This was found to be ineffective. After trying different dilutions and adding NH₄ to remove the formed NO₃, it proved impossible to isolate the F peak from the broader interfering NO₃ peak.
- 2) Use of ultrapure H₂O₂ to leach samples. The F peak could not be resolved from the chromatograms due to interference with a strong overlapping OH⁻ response.
- 3) Ashing – a suite of mountain hemlock foliage from Mt. Washington (Heberlein et al., 2017b) and sword fern foliage from the Lara area, as well as B and Ah horizon soils, were used to test the third method which involved ashing the samples to remove organic material in either a large kiln or an LOI (loss on ignition) oven. The LOI oven method was initially pursued to reduce the time required for ashing to keep the cost low. Samples were ashed at 300°C for 90 minutes, and a 1g sub-sample was then leached in deionized water at 60°C for two hours before filtration (0.45 µm) and F analysis by IC. This approach successfully resolved the F peak but the precision, determined from repeat analysis of NIST-1515 and NIST-1575 standards (apple leaves and pine needles, respectively), was found to be unacceptably poor. The experiment was then repeated at 200°C and 485°C. Precision was found to be worse at the lower temperature but at 485°C the organics were adequately removed and the samples showed reproducible results.

A comparison of the reproducibility for F and Cl in sword ferns at the different LOI oven ashing temperatures is shown in Table 4. Loss of F was a concern for the 485°C experiment; comparative tests between ashed and non-ashed CRMs (SARM-11, OREAS-45b, NIST 1515 and NIST 1575), analysed by KOH fusion and IC, revealed that between 30% and 50% of the leachable F appears to be lost by the 90-minute ashing process. Previously, Dunn et al. (2007) considered that about 95% of the F was lost from spruce needles by ashing at 485°C for 16 hours, so it is possible that F volatilizes in different amounts from different plant species, depending on how F is

sequestered within the plant structure. However, in the present and former studies it was found that the remaining F provided geologically meaningful information. In the following discussions, the 90-minute ashing at 485°C pre-treatment method is referred to by its ALS method code HAL-PREP01; the 16-hour vegetation ashing at 485°C is referred to as VEG-ASH01; and the combined ICP-MS/IC analytical method is referred to as ME-HAL01 (for sediments) or ME-HAL01a (for vegetation.) The final lower detection limits for these methods were F, 0.05ppm; Cl, 0.1ppm; Br, 0.02ppm; I, 0.002ppm.

Table 4: Fluorine and Cl precision on water leach after ashing swordfern samples at different temperatures.

Sample	Ashing at 485°C		Ashing at 300°C		Ashing at 200°C	
	F (ppm)	Cl (ppm)	F (ppm)	Cl (ppm)	F (ppm)	Cl (ppm)
SF-025-001	19.5	1314	ND	1171.2	ND	1152.4
SF-025-002	18.1	1348.6	15.59	1310.7	ND	1511.3
SF-025-003	17.3	1299.4	15.18	1302.8	ND	1475
SF-025-004	18.6	1313.1	ND	1156.4	ND	1538.6
mean	18.4	1318.8	7.69	1235.3	-	1419.3
%RSD	5	1.59	115.4	6.7	-	12.7
SF-050-001	5.4	1028.6	5.46	926.7	ND	1098.3
SF-050-002	5.1	994.5	ND	842.8	ND	946.6
SF-050-003	5.2	1002.1	6.36	967.5	ND	960.4
SF-050-004	5.9	997.8	ND	865.7	ND	1060.8
mean	5.4	1005.8	2.95	900.7	-	1016.5
%RSD	6.5	1.54	116.1	6.3	-	7.3
SF-095-001	16.4	604.7	19.1	465.5	ND	782.6
SF-095-002	16.8	547.6	19.4	472.8	ND	737
SF-095-003	17.1	577.5	ND	461.8	ND	746.2
SF-095-004	20.5	583.2	18.4	474.7	ND	717
mean	17.7	578.3	14.24	468.7	-	745.7
%RSD	10.6	4.07	66.73	1.3	-	3.7

Ashing samples at 485°C for either 90 minutes for soils or 16 hours for vegetation prior to a warm water leach was concluded to be the most effective method for successful analysis of F and Cl by IC.

One additional challenge in IC analysis was encountered in the Lara samples: Ah horizon soils and vegetation samples from all species had significantly elevated Cl contents, up to 3% in some cases. The very large Cl peaks on the IC make smaller F peaks difficult to resolve, which sometimes result in no detectable F, even when the sample site neighbours have significant F content. Work to establish an upper Cl limit to avoid inaccurate F results is on-going but was not finished at the time of publication of this report.

Bioleach Digestion of Ah Horizon Soils and Western Hemlock Foliage (WHF)

Separate splits of the milled needles (WHF) and sieved Ah horizon soils were sent to Activation Laboratories Ltd (Ancaster, ON – “Actlabs”) for analysis by their proprietary Bioleach method. On their website (www.actlabs.com) Actlabs states that:

“It has been proven that microbiological processes [in the subsurface] are exceptionally important. Electrochemical Redox cells mobilize metals from the mineral deposit to the surface which become adsorbed on soil particles and create unique surficial conditions that bacteria then feed upon. Bioleach digests bacteria and their proteins from the collected surficial samples to analyze for the elements related to the blind mineralization.....a 0.75 g sample is leached in a proprietary matrix at 30° C for 1 hour, and the solutions are analyzed on a Perkin Elmer ELAN 6000, 6100 or 9000 ICP/MS.”

Whereas this method was developed for soils, previous studies have demonstrated that similar responses are present in vegetation (Bissig et al., 2013).

Other Analytical Methods

A 0.5g split of the WHF was microwave-digested in nitric acid at the BCMOE laboratory in Victoria. Several different concentrations of nitric acid (HNO₃) were tested, but results of the analysis by IC later carried out at ALS, showed poor precision for Cl and below detection limit values for F. This may be because the nitric acid (NO₃ peak) masked the F peak in the chromatogram or perhaps the halogens volatilized during digestion or before they could be analyzed several weeks later. Re-digestion of the samples also failed to produce detectable concentrations suggesting that halogen loss is a likely cause. No further experimentation was undertaken with microwave digestion.

A 0.5g aliquot of the Ah horizon fine fraction was decomposed with a modified aqua regia digestion (ME-MS41L) and analyzed for 53 elements by ICP-MS. However, considering the disappointing results for halogens on Ah horizon obtained at Mount Washington (Heberlein et al., 2017b), it was decided not to analyze for halogens on this medium at Lara. Instead, B horizon samples collected primarily for pH and electrical conductivity measurements, were sieved and the halogens were determined on the fine fraction by the ME-HAL01 method after ashing at 485°C (VEG-ASH01).

Quality Control

Quality control measures employed at Lara included the collection of field duplicate samples for each sample type as well as the insertion of ‘blind’ control samples. For the vegetation, the control material was milled mountain hemlock needles from Mt. Washington (V14) that had been collected and characterised more than a decade earlier. For the Ah horizon, a bulk Ah sample from Ireland (LIM-2011) was available that had been characterised from multiple analyses. Details of the QC samples collected are summarized in Table 5 and detailed in the Appendix.

Table 5: Summary of quality control samples

Sample Medium	No. Samples	Standards		Field Duplicates
		V14	LIM-2011	
Western redcedar foliage (RCF)	88	2		8
Western hemlock foliage (WHF)	89	9		8
Douglas-fir bark (DFB)	79	2		7
Western hemlock bark (WHB)	67	9		2
Salal foliage (SALF)	17	2		0
Sword fern foliage (SF)	8	1		0
Oregon grape foliage (OGF)	8	1		0
Ah horizon	88	8	9	8

Results

Data Quality

An unacceptably high total measurement error can undermine the ability of a geochemical technique to detect mineralization by obscuring meaningful geochemical patterns (Abzalov, 2008). Sources of measurement error include: a) sampling error; b) preparation and subsampling error; and c) analytical error. Errors attributed to each stage of the sampling and analytical process are additive with sampling error, which is a measure of the representivity of a sample of the material being sampled, accounting for by far the largest proportion of the total.

Total measurement error is expressed as the average coefficient of variation, or % CV which is calculated using the following formula (Abzalov, 2008):

$$CV_{AVR}(\%) = 100 \times \sqrt{\frac{2}{N} \sum_{i=1}^N \left(\frac{(a_i - b_i)^2}{(a_i + b_i)^2} \right)}$$

Where a and b represent the original and duplicate analyses and N the number of duplicate pairs. Values can range from 0%, when duplicate pairs have identical concentrations, to an upper value of 141.21% (i.e. the square root of 2) where duplicate results exhibit maximum differences. For the purposes of this study, values of below 20% indicate good data quality; between 20 and 30% acceptable quality; between 30 and 50% marginal quality; and over 50%, poor quality. Elements falling in the poor category must be used with caution as their patterns are likely to be influenced by noise caused by poor reproducibility.

Precision

Table 6 summarizes the average coefficients of variation (%CV) for the different analytical methods and sample media.

Table 6. Average Coefficients of Variation for Field Duplicates

Analyte	Method	BioLeach		H ₂ O Leach	
		Ah Horizon	WHF	WHF	B Horizon
F	IC	-	-	50.94%	67.57%
Cl	IC	-	-	28.39%	45.41%
Cl	HPLC-IC			43.43%	
Cl	ICP-MS	-	-		
Br	HPLC-IC			57.53%	
Br	ICP-MS	21.78%	13.98%	30.30%	37.55%
I	HPLC-IC			82.50%	
I	ICP-MS	23.05%	7.24%	38.89%	29.89%
NH ₄	HPLC-IC	-	-	20.84%	-
PO ₄	HPLC-IC	-	-	34.51%	-
SO ₄	HPLC-IC	-	-	45.76%	-
pH	Field				9.08%
pHa	Field				6.50%
Conductivity	Field				36.72%

¹ Method HA-L01a

Data Presentation

Maps in the following pages show kriged data using a minimum curvature representation (Surfer v.14). Colour gradients are based upon progressive percentiles:

- Purple – >96th percentile
- Red – 93rd-96th percentile
- Yellow – 87th-93rd percentile
- Green – 75th-87th percentile
- Blue - 50th-75th percentile
- Lilac – 25th-50th percentile
- White - <25th percentile

The complex steep topography is not commented upon, but may play a role in dispersion patterns of some elements, especially in B horizon soils, although it is considered likely that the halogens migrate vertically from a buried source. The only B horizon data obtained were for the halogens.

Soil pH and Electrical Conductivity (Appendix – Table A2)

Table 7 presents summary statistics for the pH and electrical conductivity measurements; results for IDH and electrical conductivity are shown in Figure 8.

IDH is sensitive to the presence of remobilized carbonate in the soil. Smee (2009), Hamilton et al., (2004a, b) and Heberlein and Samson (2010) document how carbonate can be redistributed in the soils over a buried sulphide source. Oxidation of sulphides results in the release of hydrogen ions that migrate to the surface to form localized zones of acidity in the upper parts of the soil profile over the sulphide body. pH sensitive minerals, such as carbonates, become unstable in the acidified environment and migrate laterally to reprecipitate around the margins of the sulphide zone. The reprecipitated carbonate is more highly reactive than background carbonate and is susceptible to rapid dissolution in a weak acid solution. Soil pH measurements take advantage of this phenomenon. By comparing the differences in hydrogen ion concentration in acidified and

non-acidified solutions (as IDH), increases in buffering capacity caused by the reprecipitated carbonate halo may be identified.

The IDH results (Fig. 8 – left) appear to show an annulus of elevated values surrounding the surface trace of the Coronation trend. This type of response is consistent with the expression of blind sulphide mineralization. Unfortunately, the IDH response is complicated by the presence of other sulphide bearing horizons to the north of the Coronation trend. None of these appear to have similar IDH response. Furthermore, the Coronation zone response closes off to the W where the most important mineralization occurs. High IDH values in the NE part of the grid, on the slopes E of Solly creek, are unexplained.

Electrical conductivity patterns (Fig. 8 – right) are not very compelling. Soils are expected to display elevated conductivity values around the edges of a blind sulphide source (Hamilton, 2004a). No such pattern can be identified with confidence in our results. Patterns show no spatial relationship with the sulphide horizons and we conclude that they are caused by background variations. Highest values all occur on or close to creeks, suggesting that elevated conductivity may be an expression of conductive surface water. The strong response on the trend of the 262 horizon is unexplained.

Table 7: Summary statistics of pH and Electrical Conductivity measurements.

	N		Mean	Std. Dev.	Minimum	Percentiles						Maximum
	Valid	Missing				25	50	75	87	93	96	
pH (60sec)	81	0	4.83	.54	3.93	4.37	4.76	5.19	5.49	5.64	5.86	6.52
pHa	81	0	4.24	.35	3.73	3.94	4.22	4.44	4.67	4.96	5.06	5.32
Conductivity	81	0	26.13	9.70	7.80	19.55	24.20	30.25	37.99	45.33	47.26	54.30
Cond_RR	81	0	1.08	.40	.32	.81	1.00	1.25	1.57	1.87	1.95	2.24
H+	81	0	.000027	.000027	.000000	.000007	.000017	.000043	.000065	.000077	.000091	.000117
H+a	81	0	.000074	.000047	.000005	.000036	.000060	.000116	.000140	.000155	.000155	.000186
IDH	81	0	37526	45845	8632	15647	22953	37343	63156	107451	145840	308882
IDH_RR	81	0	1.63	2.00	.38	.68	1.00	1.63	2.75	4.68	6.35	13.46

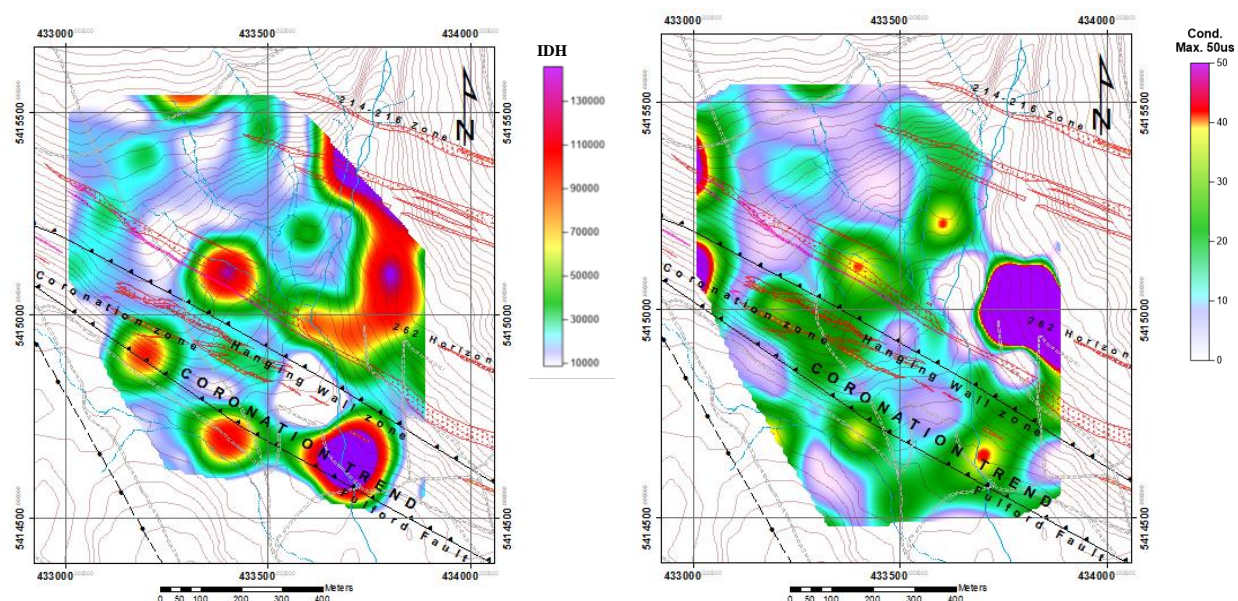


Figure 8: Soil IDH (left) and Electrical Conductivity (right)

Anions determined at the BC Ministry of Environment Laboratory - Vegetation

Limitations of the methodology are discussed in the section on analytical methods. Given the poor reproducibility of most of the ions, this section concentrates only on the data for NH_4 determined by the Auto-Analyzer, for which the RSD was 24%. The reasons for this decision are evident when the data for control V14 are reviewed. Splits of V14 (hemlock needles) were inserted at a rate of approximately one in every ten samples. Table 8 shows the considerable variability and the shifts in the data during the course of the analytical determinations for all parameters except for most of the data received for NH_4 and SO_4 .

Table 8: Analytical precision obtained on vegetation control V14. Highlighted values show anions exhibiting very high variability for the reasons discussed above.

V14	NH4 & NO3+NO2		F	Anions - Halides				Anions - OxiAnions			
	(Auto-Analyzer)		(ISE)	(Ion Chromatography)				(Ion Chromatography)			
Sample	NH4	NO3+NO2	F	Br	Cl	F	I	NO2	NO3	PO4	SO4
	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
		*	dl ~0.1	dl ~0.1			dl ~0.1	dl ~0.1	dl ~0.1		
2	n/a	n/a	nd	1.5	194.6	n/a	nd	171.5	2.2	434	211
12	n/a	n/a	nd	1.7	128.4	n/a	nd	139.7	1.7	541	456
24	111.4	nd	0.10	8.2	162.9	n/a	9.8	141.8	1.3	591	415
36	114.2	1.5	nd	7.2	260.9	n/a	nd	236.0	1.0	991	573
47	105.5	8.2	nd	13.5	88.0	n/a	1.5	18.3	2.8	1287	318
51	98.9	7.7	nd	14.2	86.0	n/a	1.2	4.2	6.9	1281	314
61	100.0	10.2	nd	31.2	92.0	n/a	1.6	8.8	5.5	1456	333
70	65.7	nd	nd	25.1	92.3	n/a	29.0	43.1	152.5	620	346
80	93.4	nd	nd	42.2	83.7	n/a	36.9	42.2	15.5	605	284

*Red - Unreliable due to precipitation of tannins in carrier solution.

Although analytical precision was too poor to warrant plotting all the data an idea of the range of concentrations can be obtained by considering some basic statistics (Table 9).

Table 9: Range of concentrations obtained from the analysis of dry western hemlock needles.

			N	Percentiles									
			Valid	Mean	Std. Dev.	Minimum	25	50	75	87	93	96	Maximum
NH ₄	ppm	Auto Analyzer	89	27	10	10	19	25	34	40	46	49	60
NO ₃ + NO ₂	ppm	Auto Analyzer	89	13	5.5	1.8	8.9	13	16	20	21	22	25
Br	ppm	Ion chromatograph	89	11	17	0.2	1.7	5.1	13	17	46	60	94
Cl	ppm	Ion chromatograph	89	265	135	70	163	226	349	417	517	575	668
I	ppm	Ion chromatograph	89	2.4	5.1	<0.1	<0.1	<0.1	3.0	6.5	9.5	16	30
NO ₂	ppm	Ion chromatograph	89	2.3	6.0	<0.1	0.3	0.9	1.7	3.1	4.8	14	42
NO ₃	ppm	Ion chromatograph	89	9.0	5.5	0.5	5.1	7.3	12	16	18	22	27
PO ₄	ppm	Ion chromatograph	89	3507	1620	818	2306	3324	4485	5476	6247	6561	9108
SO ₄	ppm	Ion chromatograph	89	586	404	12	286	491	768	1098	1407	1567	1636

The NH₄ data for samples analyzed before and after control #70 (Table 8) yielded concentrations similar to the remainder of the data and so it is considered that there was a problem with that particular control sample. A plot of the NH₄ results from analysis of the dry western hemlock foliage is shown as Figure 9. Distribution patterns do not appear to show any clear relationship to the known mineralization. Highest concentrations are in the southeast, south of the Fulford Fault, over sediments of the Nanaimo Group. Of note, is that there is a circular 'low' of NH₄ concentrations in the centre of the survey area, in an area having elevated levels of commodity elements and some halogens in several sample media.

Given the problems encountered with the vegetation samples and the budget available for the project, it was considered that analysis of the Ah samples for anions determined by IC and the Auto Analyzer, given their organic-rich nature, was not warranted without further analytical research so the only data for Ah are for multi-element suites (after aqua regia and Bioleach digestions) and some separate determinations for the halogens.

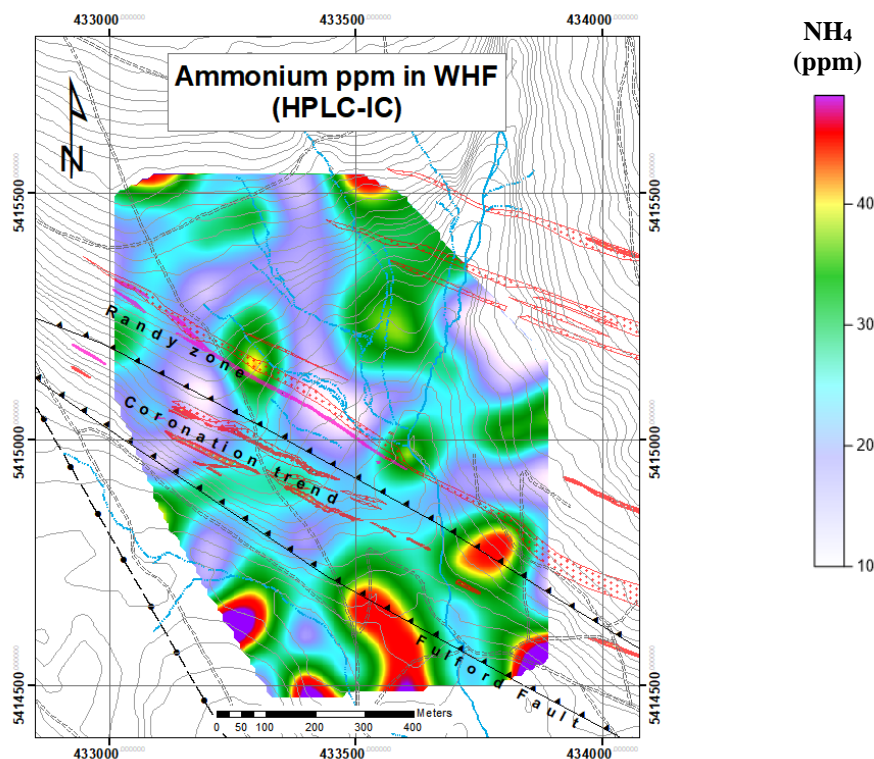


Figure 9: Ammonium in dry western hemlock needles.

Miscellaneous Species

HPLC-IC

To establish the relative halogen contents of common plant species in the survey area, and thereby establish their potential value to mineral exploration, samples of foliage and/or bark from six species were collected at approximately every fifth sample station (multimedia sample stations shown on Fig. 7). Not all of the selected species were present at all of the designated multimedia sites, but there were sufficient to establish a general picture of halogen uptake. Table 10 shows comparisons of the NH_4 and F concentrations. Clearly, swordfern and Oregon grape accumulate significantly higher levels of NH_4 than the other tissues tested. The F content of swordfern was significantly higher than other tissues, which all yielded concentrations close to or below the DL of 0.1 ppm F. The halogens and anions (NO_2 , NO_3 , NH_4 , SO_4 and PO_4) were tested on all species, but, as noted above, significant complications in the analysis precluded obtaining meaningful results. Variable tannin content of the different species and other complex organic compounds (as discussed above) resulted in highly variable results with interferences on the ion chromatograph that could not be resolved without substantial research which was beyond the scope of this project. All that can be said is that NO_2 levels (not shown) were far higher in the foliage than the bark. In the foliage, concentrations followed the trend $\text{salal} > \text{Oregon grape} > \text{redcedar}$ with concentrations in the 10s ppm, and these were substantially higher (by more than an order of magnitude) than in the bark of either western hemlock or Douglas-fir. However,

NO₃ levels were similar in all types of tissue with concentrations mostly <10 ppm and only the redcedar foliage yielded >25 ppm.

Table 10: Concentrations of NH₄ and fluorine in six (dry) tissues.

Sample medium	N	NH ₄ (Auto Analyser)			F (Ion selective electrode)		
		Average ppm	Min. ppm	Max. ppm	Average ppm	Min. ppm	Max. ppm
Salal foliage	16	<1	<1	<1	<0.1	<0.1	0.13
Swordfern foliage	8	68	40	120	31.6	15	45
Oregon grape foliage	8	80	70	96	<0.1	<0.1	0.17
Western redcedar foliage	17	25	13	37	<0.1	<0.1	0.13
Douglas-fir bark	17	15	10	27	<0.1	<0.1	<0.1
Western Hemlock bark	10	17	13	23	<0.1	<0.1	<0.1

Halogens in Vegetation Ash

The same samples of miscellaneous species were analyzed for their relative abilities to accumulate halogens. After considerable experimentation, it was found that samples needed to be reduced to ash (485°C) prior to analysis because of the unresolvable organic peaks by IC in the un-ashed material. Table 11 summarizes the data and shows the vastly different concentrations of halogens in different tissues from different species. It should be noted that in Table 11 the values are expressed as concentrations in ashed tissue, and the ash yields are shown in the right-hand column.

Of note are:

1. Very high concentrations of F in the swordfern, relative to the other sample media, confirming the observation of relative enrichment of F in dry tissue, when determined by ISE.
2. Very high concentrations of Cl in the swordfern and salal leaves relative to the other sample media
3. Bromine is moderately higher in swordfern and salal compared to other media.

Table 11: Average halogen concentrations in vegetation ash¹.

Medium	N	I_ppm	Br_ppm	F_ppm	Cl_ppm(IC)	Cl_ppm(MS)	Ash_yield %
Douglas-fir bark	16	0.27	44	1.4	1934	2178	1.0
Oregon grade foliage	7	0.98	26	3.4	1807	2548	2.4
Western redcedar foliage	17	0.39	32	1.95	6059	5959	4.3
Swordfern foliage	8	1.43	78	387	17009	>27000	4.6
Salal foliage	16	0.4	54	<0.05	22141	28066	4.0
Western hemlock bark	8	0.16	48	20.2	1528	1921	1.2
Western hemlock foliage	40	0.4	18	2.04	2180	na	3.7

¹ – Ashing done at 485°C for 16 hours

Multi-element Determinations

Aqua regia digestion of Ah soils (Appendix – Table A3)

Along the Coronation trend there are several sites with relatively high concentrations of K (presumably reflecting potassic alteration) and traces of Au (Fig. 10). There was no clear relationship of Na that might demonstrate Na depletion (not shown)

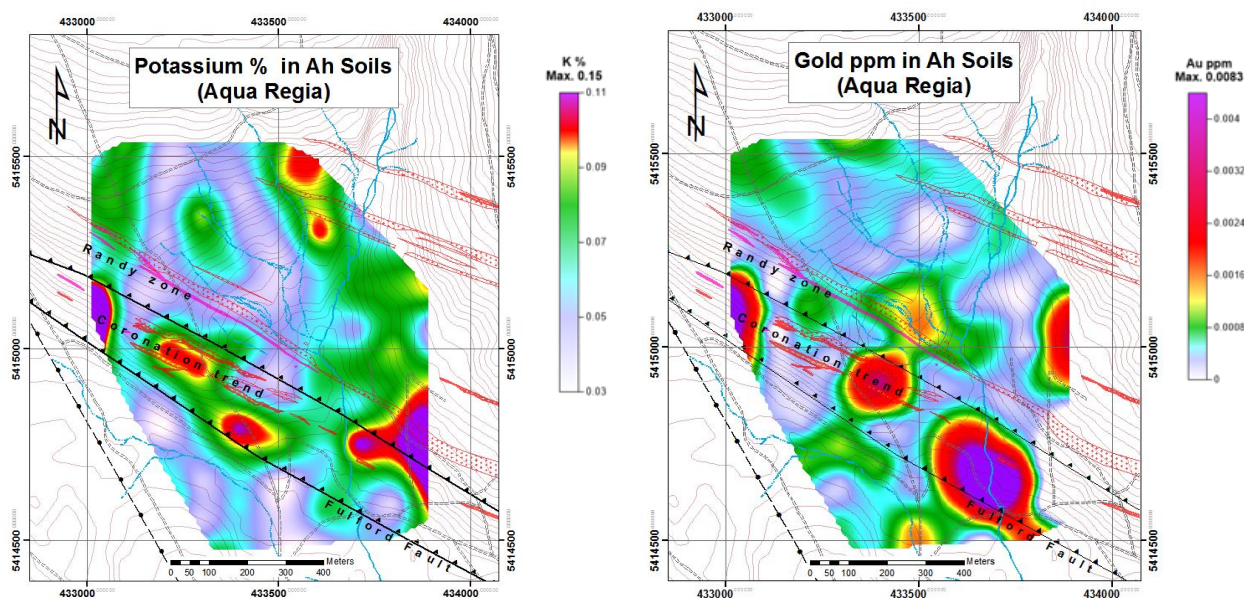


Figure 10: Potassium and Au in Ah soils (aqua regia digestion).

Many commodity elements are enriched in an area to the north of the Coronation trend that has seen very little drilling. Of note are the distribution patterns of several elements depicted in Figures 11 and 12.

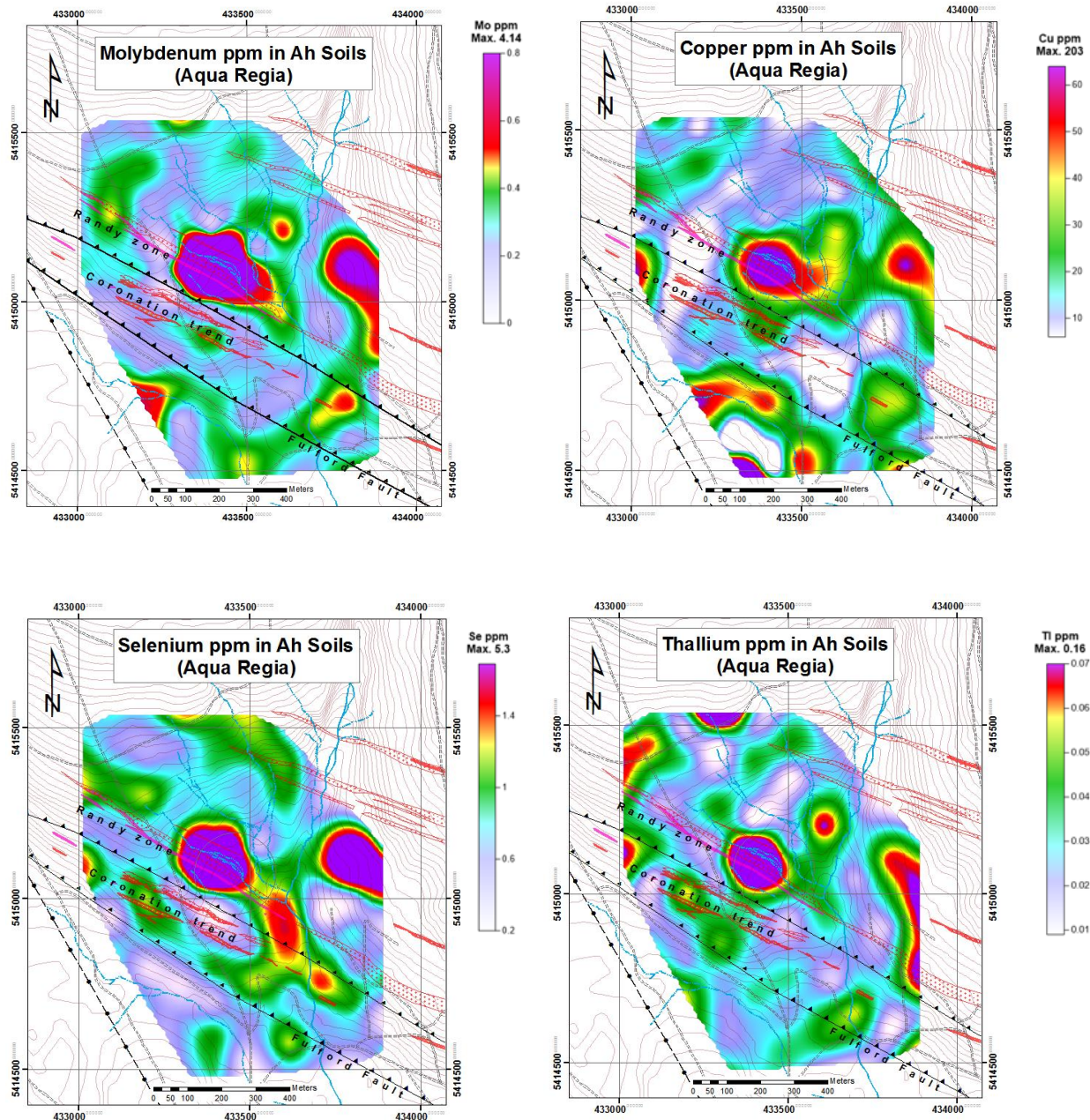


Figure 11: A comparison of metal distributions in Ah soils (aqua regia digestion) of Mo, Cu, Se and Tl in the central part of the survey area.

Zinc, Cd, Cs and, to a lesser degree, As have coincident anomalies (Fig. 12).

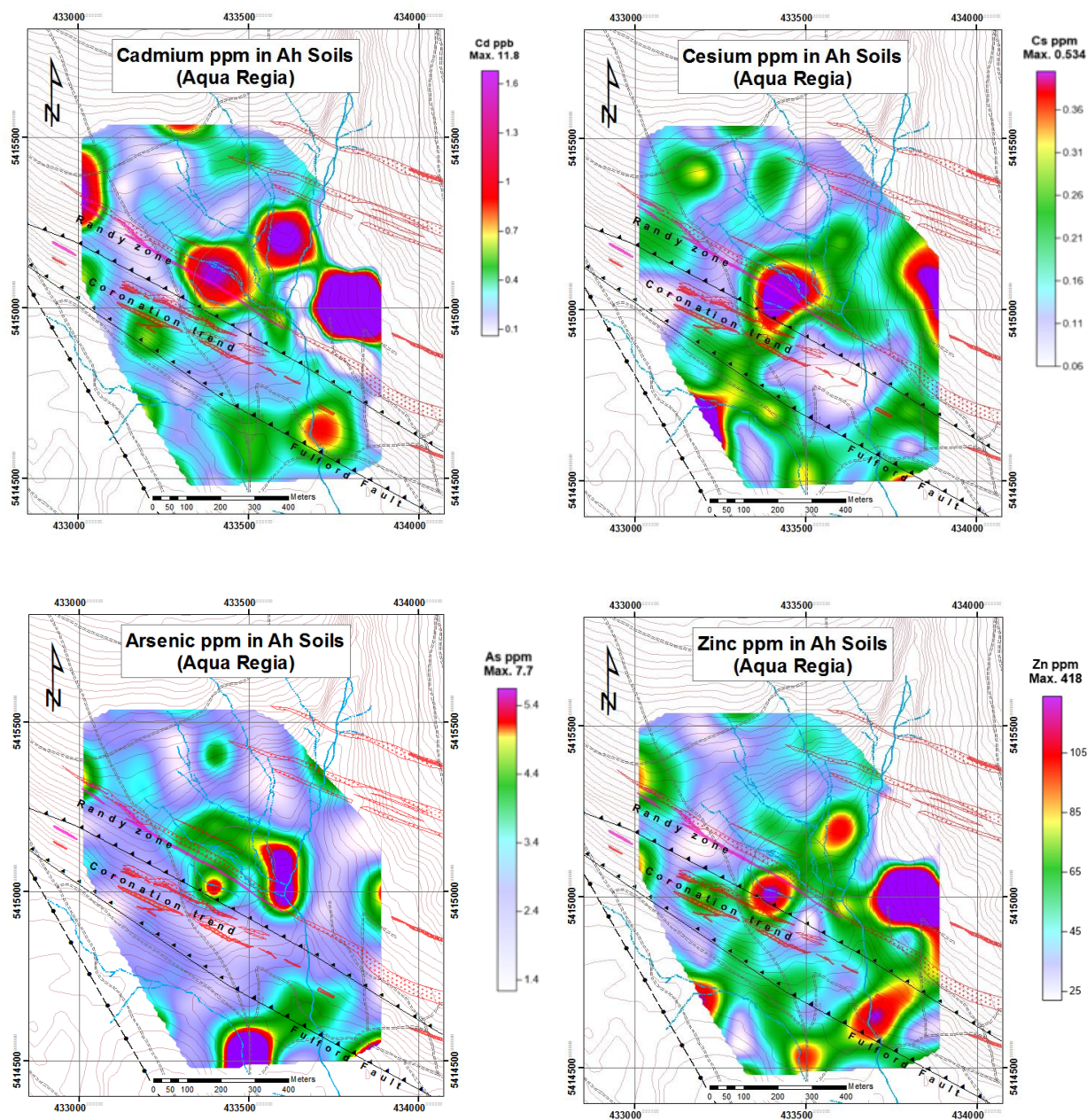


Figure 12: Cadmium, Cs, As and Zn in Ah soils (aqua regia digestion).

Of note is that close to the eastern margin of the survey Mo, Se, Tl, U, Cs and Cd have coincident enrichment (Figs. 11 and 12) along with by far the highest concentration of Zn.

Lead and Sb exhibit a different pattern with enrichments occurring in the northern part of the survey area (Fig. 13).

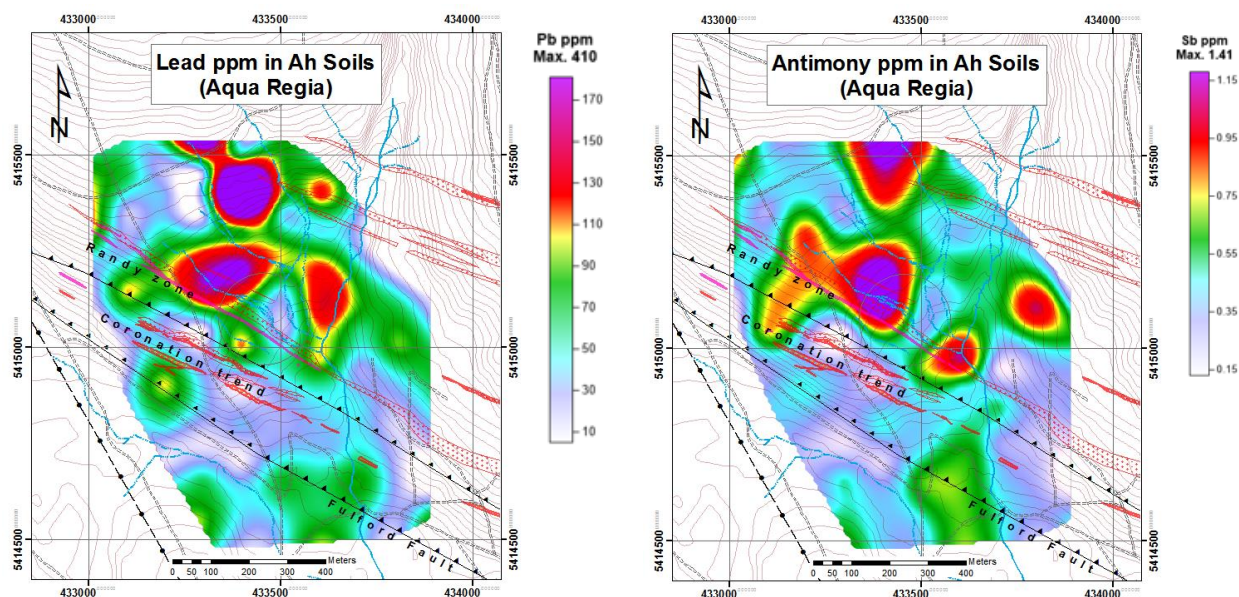


Figure 13: Lead and Sb in Ah soils (aqua regia).

The relationships of some of these anomalies, notably in the central area, are discussed later in relation to halogen distribution patterns.

B Horizon Soils (Appendix – Table A4)

Samples collected from the upper B horizon for pH and conductivity measurements were digested in warm water and the halogens determined using the methods developed at ALS (Fig. 14). No additional analytical determinations were conducted on the B horizon samples.

Clearly, the distribution patterns of Br and I are very similar with the central multi-element anomaly coincident with both elements and in the same location of many commodity element enrichments in the Ah horizon (Figs. 11 and 12). Chlorine presents a considerably more diffuse pattern, whereas F enrichments are peripheral to the Br and I suggesting possible zonation of the halogens outward from the central zone of enrichment.

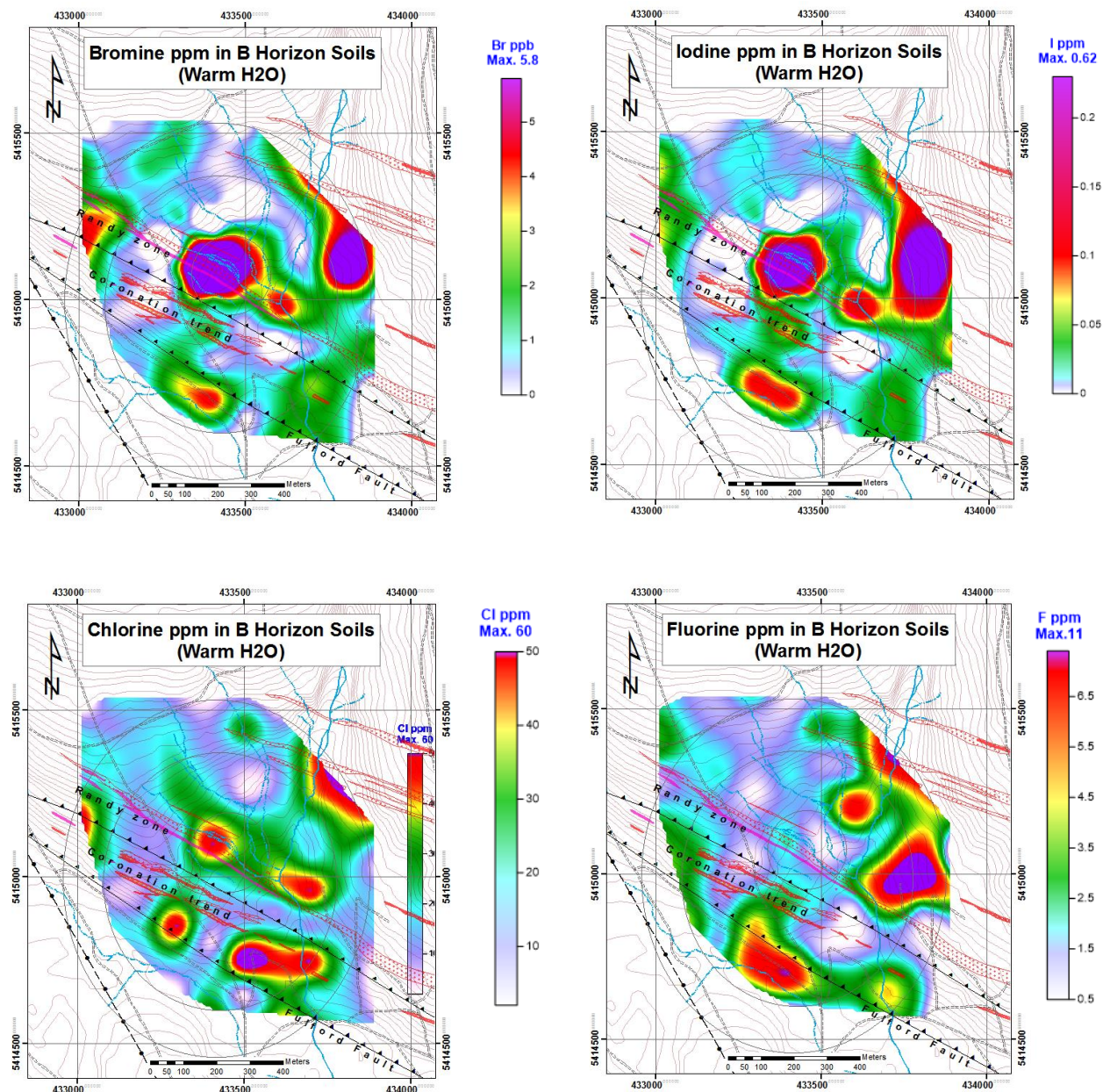


Figure 14: Halogens in B horizon soils – warm water leach.

Warm water leach of ashed western hemlock needles (WHF; Appendix - Table A5)

Halogen determinations on WHF were made only on samples that were reduced to ash by controlled ignition at 485°C, thereby eliminating the interferences from organic matter. Because most of the material had been used up on repeated experimentation, only 73 of the 88 determinations warranted plotting because ash yields from the remainder were too low (<0.2 g) to obtain acceptable precision, and a few samples reported with spuriously high ash yields have been omitted.

Each halogen generates a similar but subtly different distribution pattern (Fig. 15). Chlorine and Br show rings of relative enrichment around the Coronation trend. Iodine is even more focused with a tighter ring of anomalous values. Precision of the data for F was poor with several samples yielding concentrations below the detection limit of 0.5 ppm F, yet a focused ring structure is apparent – more or less peripheral to the I. However, the results for F should be treated with caution since they may not be repeatable.

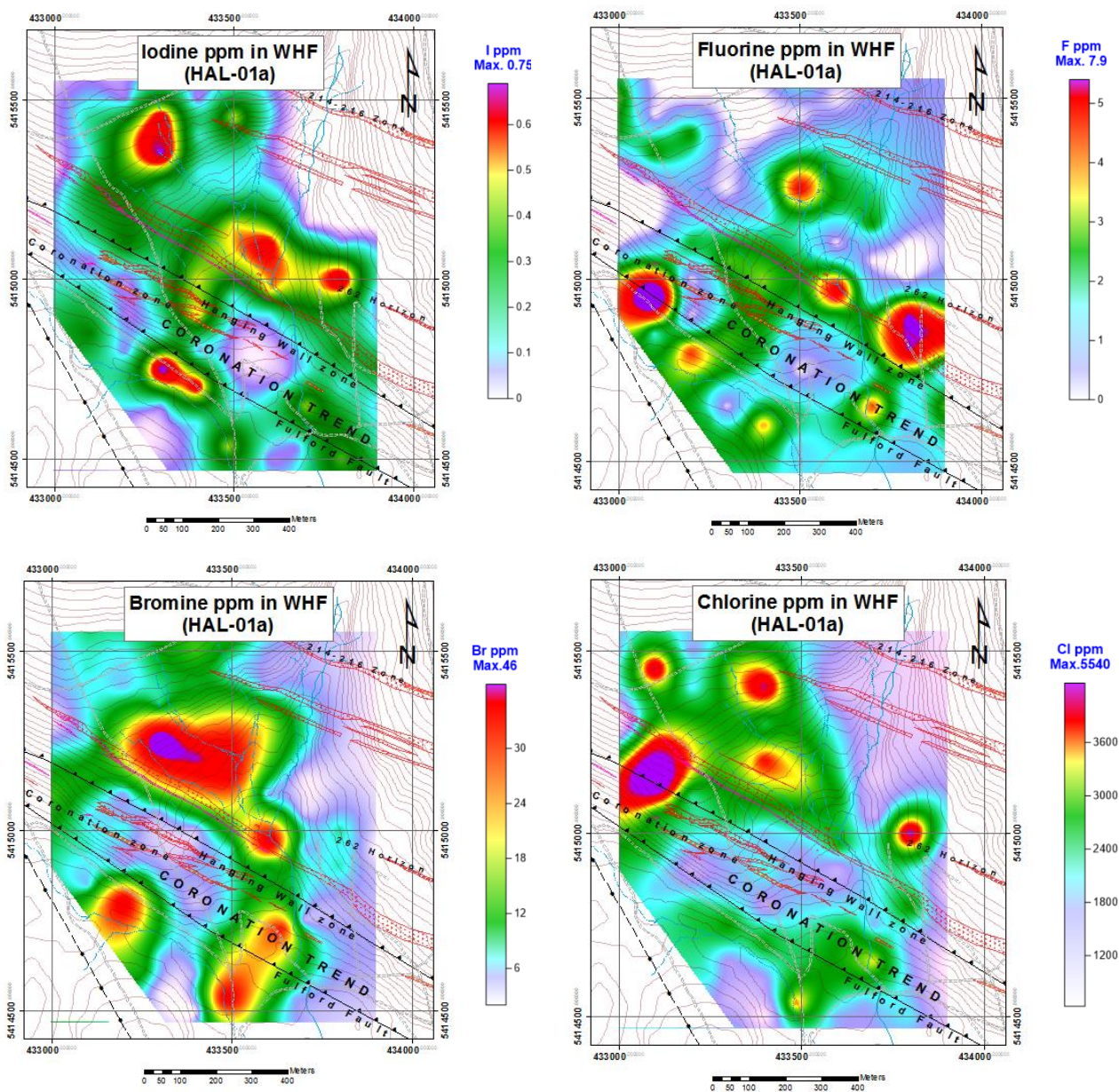


Figure 15: Halogens in ashed western hemlock foliage (ME-HAL01a).

Bioleach – Multi-element data

Bioleach Digestion of Ah soils (Appendix – Table A6)

Splits of all sieved Ah soil samples were sent to Actlabs for Bioleach and multi-element analysis. This partial leach has the advantage for the present survey that data for Br and I are part of the analytical package. All results are concentrations in the dried -80 mesh fraction. Table A7, Appendix 1, shows data listings with several spreadsheets showing the quality controls (blind duplicates, field duplicates and laboratory controls) along with a statistical summary on the last spreadsheet. The analytical precision for the Bioleach was very good with most elements yielding RSDs of less than 10%. Only Au, Bi, Li, Ru and W had RSDs >20%. For Br and I the RSDs were 5% and 9%, respectively.

Bioleach - Alteration, Commodity and Pathfinder Elements

Mineralization is associated with Na depletion and K metasomatism. Sodium is not part of the Bioleach analytical package, but K is included. The distribution of K shows enrichments along the trend of the Coronation mineralization (Fig. 16) and other sites over felsic volcanic rocks.

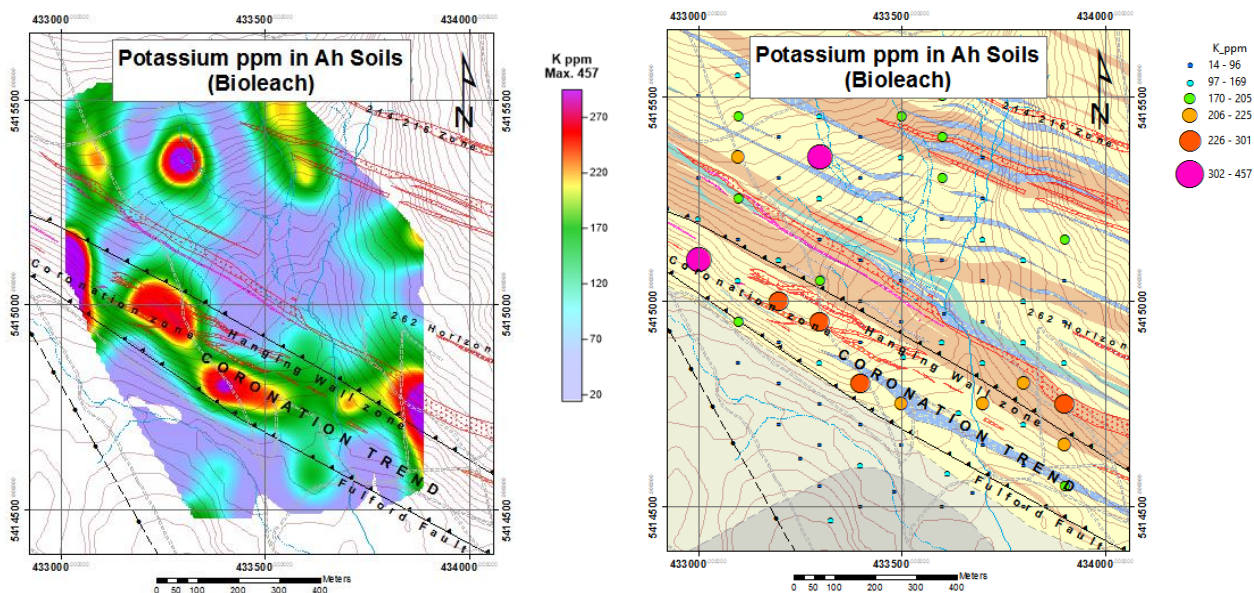


Figure 16: Bioleach - K in Ah soils.

Of the commodity metals that comprise the Coronation zone mineralization (Ag, Cu, Fe, Pb and Zn), only Zn shows a moderately good relationship to the known zones (Fig. 17). There is, in addition, an area to the east where some of the highest values occur over felsic volcanics forming steep slopes above Solly Creek. This is apparent, too, in the aqua regia digestion of the Ah soils (Figs 11 and 12).

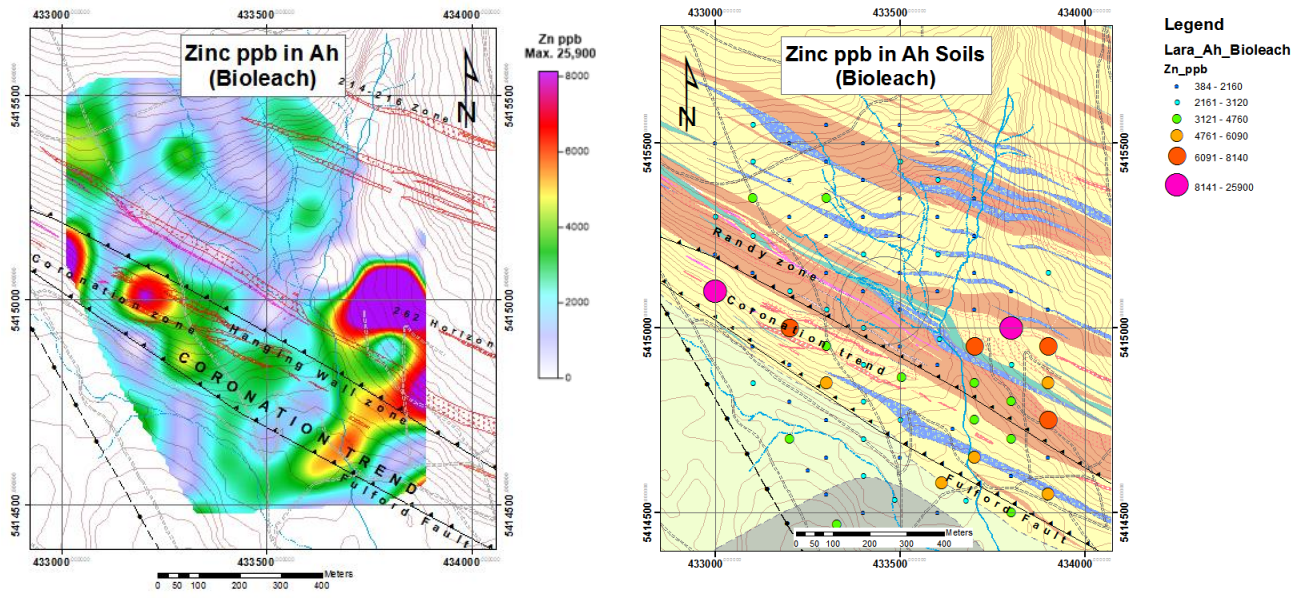


Figure 17: Bioleach - Zn in Ah soils.

Bioleach – Halogens in Ah soils

Bromine and I are part of the suite of elements determined by Bioleach. As indicated earlier, the precision obtained for these elements was excellent – less than 10% RSD. Figure 18 shows the gridded Br results alongside a proportional dot map of the same data on the geological base. A strong anomalous zone is evident in the centre of the survey area, to the north of the Coronation trend on the west side of the gully incised by Solly Creek. In addition, there is halo of areas some 200 m distant that have relatively high Br concentrations.

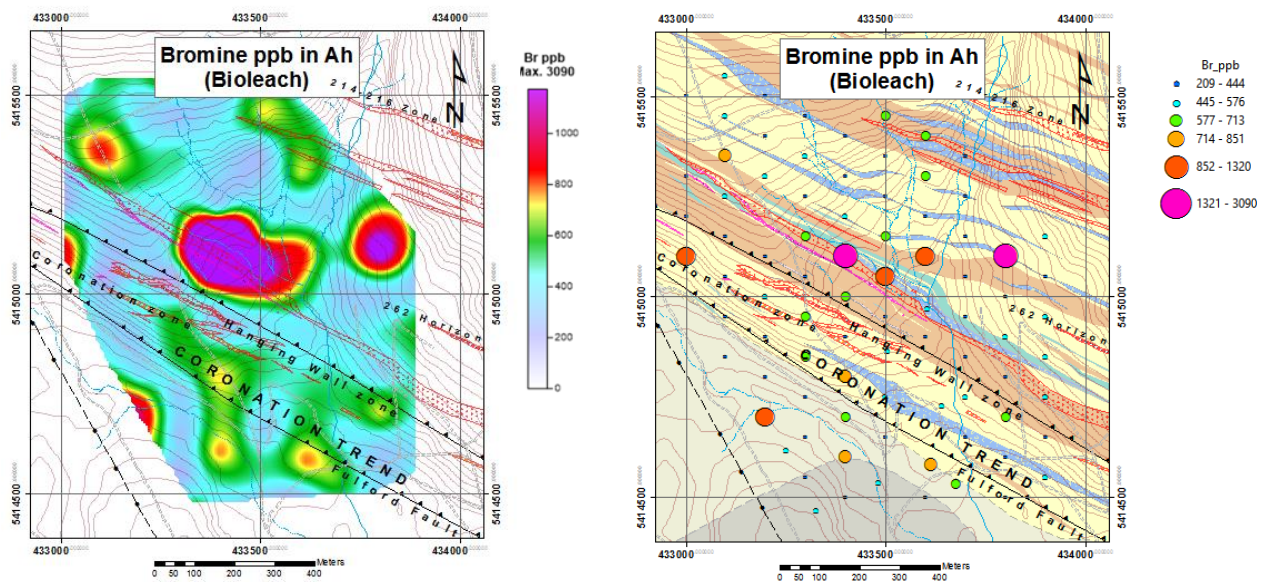


Figure 18: Bioleach - Br in Ah soils.

Iodine (Fig. 19) exhibits a similar pattern - a central zone of enrichment with a diffuse halo of variable I enrichment.

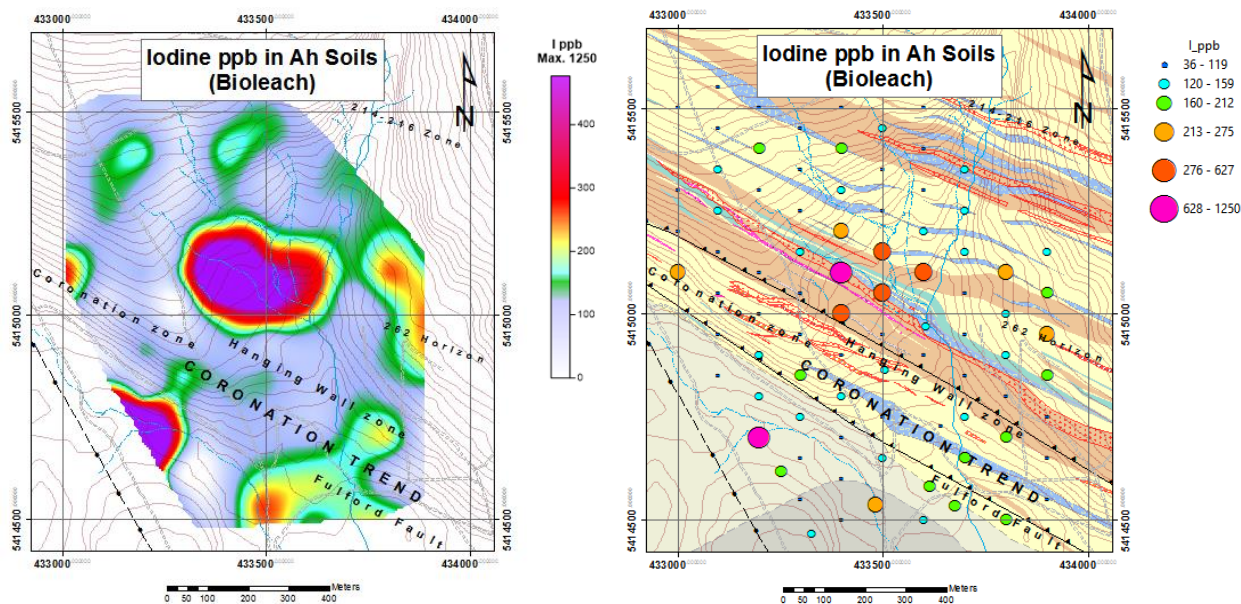


Figure 19: Bioleach - I in Ah soils.

Figures 18 and 19 demonstrate that Bioleach extraction of the Ah soils gives rise to similar distribution patterns of I and Br with the same prominent central anomalous zone, and halos of lesser enrichment. An interpretation of this pattern is that the two halogens could represent an aureole of outward diffusion over the northeast-dipping Coronation trend of mineralization. The source of the central anomaly is not known but could be related to a yet undiscovered zone of mineralization that might not be Zn-rich, given the lack of an associated Zn anomaly in this area. The section on multi-element analysis of the Ah horizon expands on this hypothesis.

Western Hemlock Foliage (WHF) Bioleach (Appendix Table A7).

Commodity and Pathfinders elements

Bioleach was performed on all the western hemlock foliage samples. Figure 20 shows that the alkali metals Rb and Cs are enriched in the central part of the survey area where there are also enrichments of Br and I in the Ah horizon samples.

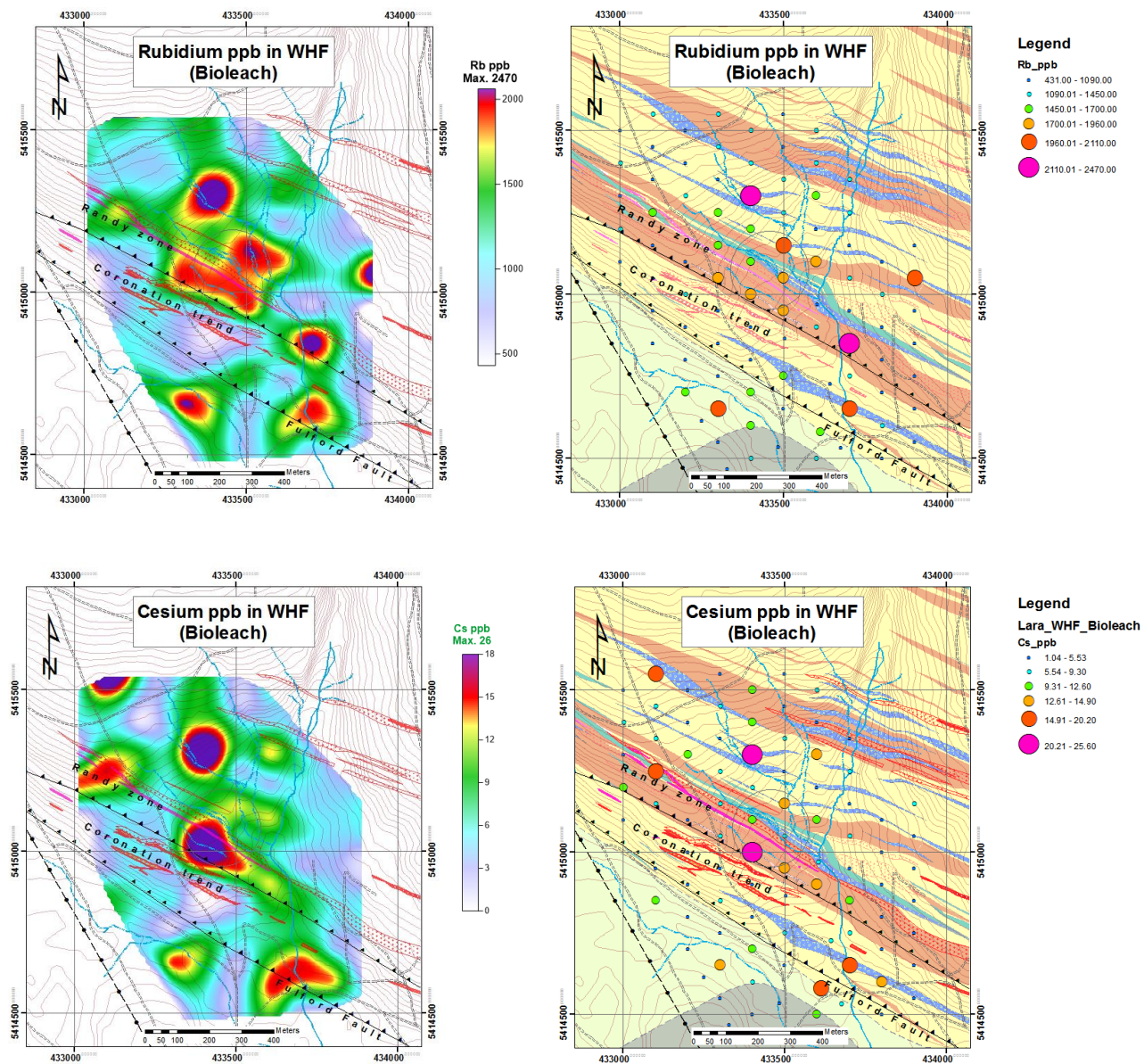


Figure 20: Bioleach - Rb and Cs in western hemlock foliage.

Zinc enrichments follow the outer margins of the faulted block comprising the Coronation trend (Fig. 21).

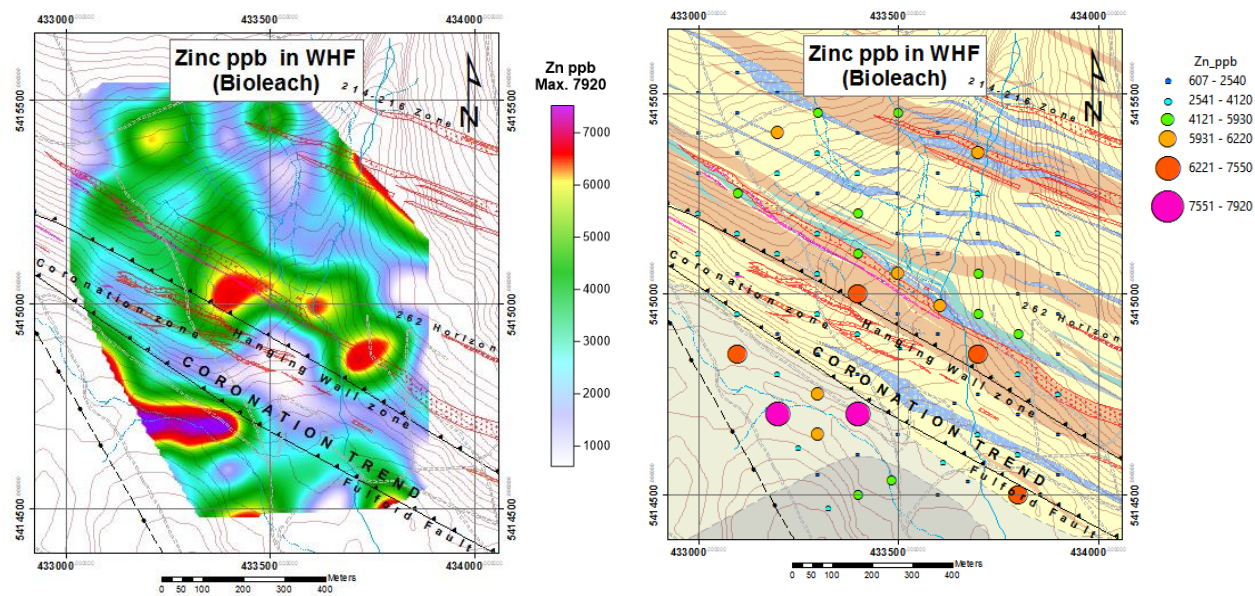


Figure 21: Bioleach – Zn in western hemlock foliage.

Bioleach – Halogens in western hemlock foliage (WHF)

The signature of Br in the WHF shows relative enrichments in the eastern part of the survey area, whereas I appears unrelated to the Br (Figs. 22 and 23).

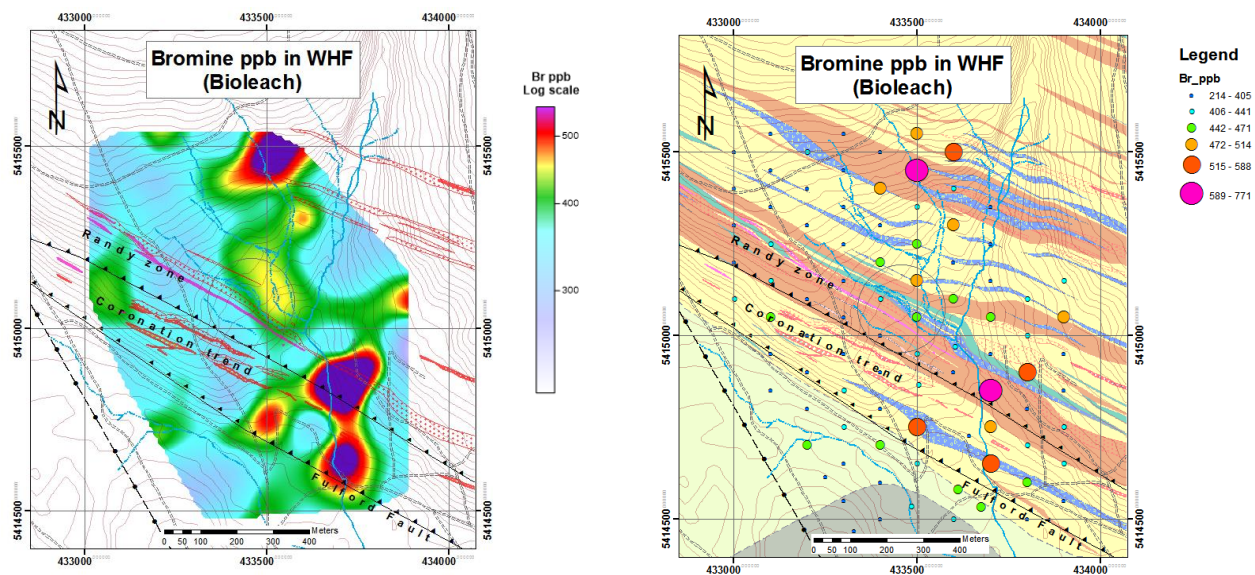


Figure 22: Bioleach - Br in western hemlock foliage.

When the patterns of I in WHF are compared to those of I by Bioleach in the Ah soils, it appears that the former forms an annulus around the central anomaly in the soils, where many elements are concentrated (Fig. 23)

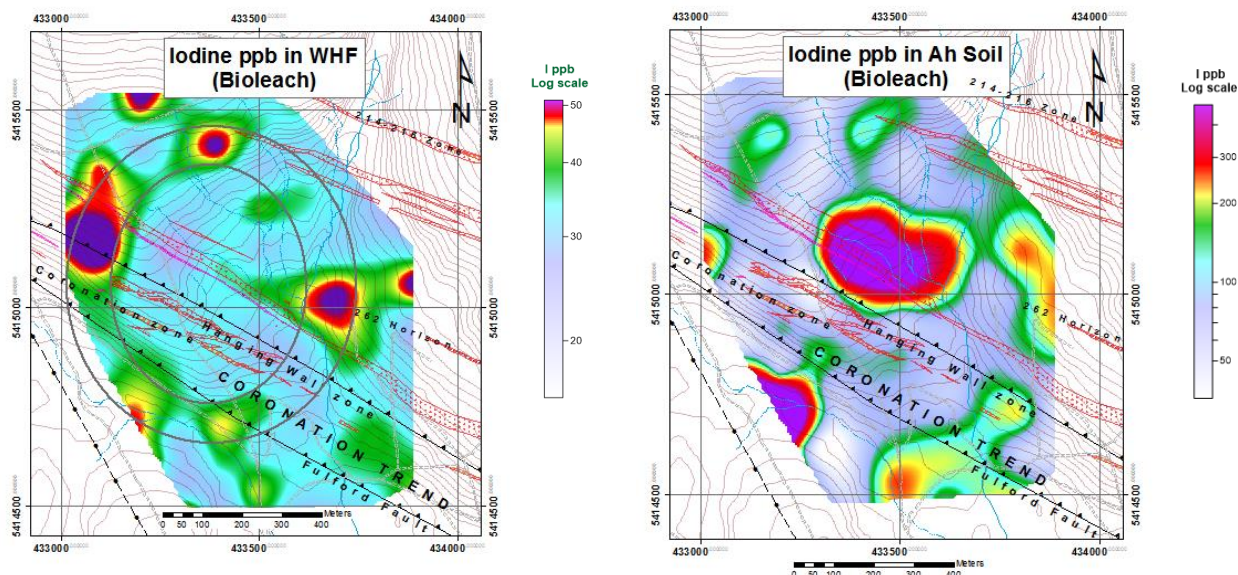


Figure 23: Bioleach - I in western hemlock foliage.

Discussion

Extensive analytical research and experimentation has defined numerous problems with regard to analytical interferences in the organic-rich media and the great difficulty (and sometimes impossibility) in isolating elemental peaks on the Ion Chromatograph. Consequently, it was concluded that High Performance Liquid Chromatography and Ion Chromatography (HPLC-IC) were not suitable for most of the required elements and compounds given the constraints on developing rapid and cost-effective methods with good precision.

Initial tests were warm water leachates on approximately 200 vegetation samples. They were analyzed by HPLC-IC for Cl, Br, I, PO₄ and SO₄ at the laboratories of the BC Ministry of Environment in Victoria, BC. The same solutions were analyzed on an Auto Analyzer (an automated analyzer using continuous flow analysis (CFA)), for NO₃ and NH₄ and for F using an ion selective electrode (ISE). Only the NH₄ proved to have adequate analytical precision to be of use for this survey, for a list of reasons that are discussed.

For the halogens, it appears that the optimal procedure at this time is to first reduce the organic media to ash by controlled ignition for a set period of time. The Ah horizon soils can be reduced to ash by ignition at 485°C for 90 minutes, whereas the vegetation samples require fully ashing at the same temperature for 16 hours. This preparation of the samples has provided data with acceptable precision for most of the halogens, with F remaining the element presenting the greatest problems.

The partial leach method 'Bioleach' provided data with the best analytical precision, but the multi-element technique can only produce results for Br and I – not for Cl or F.

The significance of I and Br for indicating deep ore deposits is discussed in Trofimov and Rychkov (2004). They provide several examples of the exceptional migrational abilities of I and Br, and “show these elements to be highly effective in exploring for deeply buried ore bodies” “within all deposits studied, iodine and bromine occupy the position most distant from ore

bodies. This extreme zonal position makes it possible to use these elements as very effective indicators of hidden ore deposits". As an example, they show concentrations of I in soils developed on sandy loam that blankets a Cu porphyry system and the Rabbit's Ear-type anomaly that results along a profile, and indicate that this is a halo effect around discrete mineralized bodies (Fig. 24). They show that I and Br occupy the extreme outer position in relation to ore deposits, and they are the most useful indicator elements for deep-seated blind mineralization.

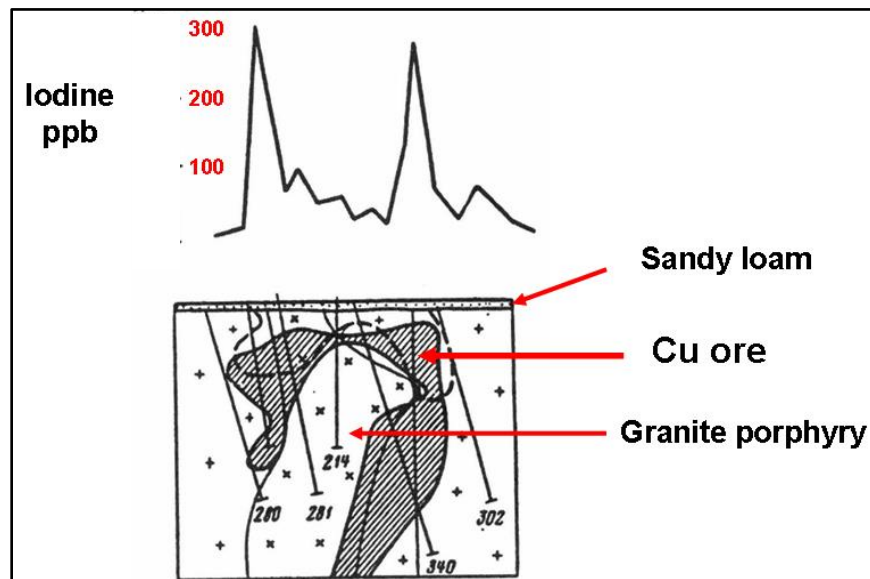


Figure 24: Iodine in soils over the Karatas Cu porphyry deposit, Kazakhstan. Annotated in Dunn et al. (2007) after Trofimov and Rychkov (2004).

In the final chapter of the book they conclude that “*Regional and local hydrothermal metamorphism has created significant difficulties in interpreting primary iodine and bromine halos used to explore for hidden ores. Halos formed by mobile iodine and bromine, instead of by bulk concentrations, may be useful in geochemical exploration. Use of mobile forms allows the determination of iodine and bromine concentrations in intergranular films, and it considerably increases the depth of exploration and decreases exploration costs. Studies have shown that it is possible to explore to 1,000 m depth*”.

In the current study, there are considerable differences in the distribution patterns of Br and I in the various sample media investigated. The highly variable underlying geology and complex array of Quaternary deposits, along with multiple zones of mineralization have made the Lara area extremely challenging for isolating distribution patterns of the halogens as they relate to mineralization. The differing signatures of the media analyzed demonstrate the complexity of the problem. Nevertheless, there are certain consistent patterns:

1. B horizon soils exhibit pronounced anomalies in Br and I in the centre of the survey area, just north of the Coronation trend. Distribution of Cl and F are different and their significance not obvious. Coincident with these anomalies, in the aqua regia digestion of Ah horizon soils there are enrichments of Mo, Cu, Se, Tl, Cs, Cd and Zn with slightly elevated levels of As. This suite of elements is characteristic of VMS mineralization. Other elements commonly associated with VMS deposits are Pb, Sb, Bi, Ag and Sn, all

of which are relatively enriched to the north of this main suite. Plots are shown of Pb and Sb in Figure 13, and data for all elements are listed in the Appendix (Table A3).

2. Bioleach results for Br and I on the Ah horizon show strong anomalies coincident with the suite of elements shown above to be enriched in aqua regia digestions of the Ah horizon, and also coincident with patterns of halogen signatures in the B horizon (warm water leach).
3. Warm water leaching of dry WHF, however, shows different patterns. Ammonium is depleted in the centre of the survey area where the soils show multi-element enrichments. The halogens determined from a water leach of ashed WHF tend to show annular anomalies – especially Br with the annulus for Cl being more diffuse and marginal to the outer limit of the Br halo. Iodine and F are more difficult to interpret.
4. Bioleach of the dry WHF presents a picture of a discontinuous annulus of I (Fig. 23) distant to the central multi-element and halogen anomalies shown by the soils.
5. Possibly the soil results are more meaningful at the scale investigated, since I variations may be attributable to the role that I plays in plant metabolism. It is involved in enzyme activity, osmotic regulation and stomatal movement (summarized in Dunn, 2007). Conversely, Br is not known to be essential for plant metabolism and so it could be conjectured that a positive response in vegetation may be more directly related than I to halogen enrichment associated with mineralization, and therefore may account for the differences observed in this study. It is noteworthy that the patterns of the halogens in soils appear to be more readily interpreted as being related to known VMS mineralization, than the halogens in the plant tissues.

A few samples of other plant tissues (bark and foliage) from the dominant conifers and some understory plants showed elevated concentrations of:

- a) NH_4 in swordfern and Oregon grape;
- b) F in the swordfern;
- c) Cl (>2% in ash) in swordfern and salal.

Ferns could be a useful sample medium for establishing patterns of relative concentrations of F in the absence of other species.

Summary and recommendations

Problems persist in obtaining stable low-level halogen data from organic-rich media. Ashing of samples prior to analysis goes a long way to circumventing these problems. The same problems apply to obtaining data for a range of other volatile compounds, with only NH_4 having adequate precision in the western hemlock foliage (WHF). Continuing research is required to refine the methodology, especially for F.

Halogen distribution patterns are mostly different in WHF from those in soils. The source of the multi-element anomaly in the centre of the survey area (that is coincident with Br and I enrichments in soils) is unknown since it appears that this area has not been drilled. If it transpires that this anomaly is not directly related to mineralization, then it would seem that the WHF patterns are the more meaningful in this environment. More research and experimentation is required over different styles of mineralization before the preferred sample medium and

analytical method can be firmly established. To this end, the second phase of this study discussed in the accompanying report (Heberlein et al., 2017b) provides more conclusive data on the processes giving rise to surface halogen anomalies over a Au-Ag-Cu epithermal system close to the surface.

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