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**Halogens and Other Volatile Compounds in  
Surface Sample Media as Indicators of  
Mineralization. Part 2: Mount Washington  
Epithermal Au-Cu-Ag Prospect, Vancouver  
Island, BC (NTS 092F/14)**

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## Executive Summary

A 1990 biogeochemical study carried out at Mount Washington by the Geological Survey of Canada identified a strong geochemical signal for Au, Ag and Cu and certain pathfinder elements over the known mineralization. A positive Br response was also identified in yellow cedar bark ash (*Chamaecyparis nootkatensis*). This observation was fundamental in the selection of Mount Washington as a location for the investigation of halogens and other volatile compound dispersion in surface media.

A sampling and analytical program was designed to collect and analyze a variety of surface media that might help in understanding mobility patterns of halogen and other volatile elements. Components of the study, from the ground up, included the burial of activated charcoal and alkaline ion exchange resin packages for three months to capture volatile anions and cations emanating from the ground; the collection of: 1) organic-rich Ah-horizon soil; 2) foliage of mountain hemlock (*Tsuga mertensiana*) - MHF; 3) analysis of archived yellow cedar bark (*Chamaecyparis nootkatensis*, collected in 1990); 4) fluids transpiring from the hemlock foliage; and 5) snow.

This study complements a parallel study of halogen signatures in soils, western hemlock foliage and several additional plant species over the Lara VMS deposit and seeks to answer some of the questions posed by that study (Heberlein et al., 2017a).

Analytical methods were similar to those at Lara, with the addition of some experimentation on ashing of soils and vegetation at different temperatures before settling on two methods that optimized the precision of the analytical data: 1) the dried –80 mesh (177 µm) fraction was digested in modified aqua regia and analyzed for 53 elements by inductively coupled plasma mass spectrometry (ICP-MS); 2) a second split was reduced to ash at 485°C for 90 minutes and the ash digested in warm water then analyzed for halogens by ion chromatography (IC) and ICP-MS; 3) milled MHF samples were ashed at 485°C for 16 hours and modified aqua regia digested prior to multi-element analysis, and another aliquot leached with warm water and analyzed for F, Cl, Br and I by IC and ICP-MS. Splits of the Ah horizon soil and milled MHF were shipped to Actlabs in Ancaster, Ontario, for analysis by their proprietary Bioleach method.

Analysis of the ion collectors was carried out using several different methods. Charcoal collectors were ashed for 16 hours at 485°C, leached in warm water and analyzed for the halogens. A 1 g split was also analyzed by ICP-MS after leaching with 25 mL of sodium pyrophosphate solution. A second 1g split was digested in aqua regia and analyzed by ICP-MS.

Halogen analysis of the resin collectors involved leaching in cold hydroxylamine hydrochloride, and multi-element analysis by ICP-MS. Chlorine, Br and I were analysed by ICP-MS after a warm water leach. Results for most elements, including Br and I, were below detection limit.

The transpired fluids and snow samples were analyzed directly for multi-elements by ICP-MS and by IC/ICP-MS for the halogens. Snow analyses were repeated after pre-concentration by evaporation to 20% volume to enhance halogen concentrations above detection limit.

In general, the analytical precision for the halogens was fair to poor, but of sufficient quality to relate distribution patterns to zones of known mineralization. The charcoal ion collectors had the best reproducibility of all media.

The principal observations on the volatile components for each medium are:

1. Ah soils – elevated halogen concentrations are mostly in areas with poor drainage (high organic content) that tend to subdue enrichments over the mineralized breccia zone. The same was noted for the Bioleach of Br and I.
2. Bioleach digestion of neither the Ah horizon soils nor the MHF provided a distinct mineralization-related signature
3. Charcoal collectors – Br and I are not enriched at the wet sites, and appear to exhibit a 'Rabbit's Ear' pattern of enrichments either side of the mineralized breccia. This was apparent from both the warm water and Na pyrophosphate leaches.
4. Resin collectors – Br shows a Rabbit's Ear response over the breccia (warm water leach).
5. Mountain hemlock foliage – there is an I response over the breccia zone that is better than Br which in turn is better than Cl. This indicates that in the MHF the halogens are responding to mineralization and not to the ground saturation, since the wet areas are not anomalous in these elements. Similarly,  $\text{NH}_4$  and  $\text{SO}_4$  show a positive response over mineralization, whereas  $\text{PO}_4$  shows a negative response.
6. Ashed bark of yellow cedar collected in 1990 and retrieved from GSC archival storage, yielded almost identical distribution patterns of Br concentrations when analyzed by INAA (1990) to the ICP-MS method on a warm water leach. Both Br and Cl yielded highest concentrations over the mineralized breccia, with some of the highest I values from the same area.
7. Most of the highest halogen concentrations in fluids transpired from the mountain hemlock needles were from sites over the breccia zone, with a consistent high, also, from an unknown source at the southernmost site.
8. The small database of snow samples shows that at the two sample stations where samples were collected from increasing depths, both Br and I have their highest concentrations close to the base of the snow pack and decrease upward. The implication is that there is a constant flux of these elements upward during the winter. A site of anomalous halogen concentrations at the southern end of the survey line is of unknown source, but it is intriguing that high concentrations of halogens occur here, too in other sample media.

General conclusions that can be drawn from these datasets are that concentrations of halogens in some media (e.g. Ah horizon soils) are influenced by the degree of water saturation and high organic carbon content. The Ah horizon samples produce no recognizable responses over the mineralized zones whereas MHF shows convincing anomalies. Organo-halogen accumulation in the poorly drained soils is overwhelming the subtler mineralized response. Mountain hemlocks are less sensitive to this process and the halogen contents of their needles thus more accurately reflect the signature of the mineralization. The most convincing dataset for reflecting the mineralization in this study comes from the fluids transpired from the mountain hemlock needles. The procedure for collecting the fluids is simple and presents a simple medium to analyze with few matrix interferences.

This project demonstrates that halogens may be used as pathfinder elements for the exploration for blind (e.g. Lara) or subcropping mineral deposits (e.g. Mount Washington). It also highlights the appropriate sample media and analytical methods to use. However, these are specific to one

forest type and surficial environment and do not encompass all potential environments in BC. More work is needed to optimize sample media in other common forest types such as the spruce, lodgepole pine or Douglas-fir forests of the interior.

Further development of the analytical methods is important if halogens are to become widely used by the mineral exploration community. Work should include further research into inexpensive low detection limit methods for determining F in organic media. This should include further development of the IC method with the aim of eliminating interferences that affect the F chromatogram peaks. Collection and certification of new control samples is necessary for other common tree and understorey species found throughout BC.

## Introduction

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, volatile compounds (mainly in the form of HF, HCl, HBr and HI) and gasses derived from them (Aiuppa et al., 2008) 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 where F, in particular, can substitute for O and hydroxyl. The heavier halogens Cl, Br and I have larger ionic radii and smaller electronegativities than F which favours coordination with large ion lithophile elements. 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, topaz, and the gangue mineral fluorite.

On exposure to surface conditions, these minerals weather and release their halogens as volatile vapours (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 many case histories that demonstrate positive responses of all these elements and other volatile compounds to zones of concealed mineralization (Al Ajely et al., 1985; Ridgway, 1989, 1991; Ridgway et al., 1990; Trofimov and Rychkov, 2004). However, the halogens have seen little or no application as pathfinder elements to the exploration for minerals in the extensively-covered terrains of British Columbia. This is because of their relative difficulty of analysis, a lack of commercially available halogen analytical packages for surficial media, case histories and cost.

## ***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 glacial 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 acceptable analytical precision and accuracy at the low concentration levels typically present in a water leach of soils and vegetation, and at an acceptable cost to mineral exploration companies.

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 or Br 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, Central B.C., demonstrated that the partial extraction techniques Bioleach and Enzyme Leach produced robust responses in Br and I over blind mineralization at the Three Firs prospect.

## ***Project Objectives***

The current project expands on the 2005 and 2013 studies by investigating halogen and other volatile compound responses 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 style of mineralization for which the halogen response has not previously been tested) that is buried by 5 to 10 metres of till; Mount Washington is a subcropping epithermal Au-Ag-Cu system with a thin veneer of colluvium. This report deals with the Mount Washington component of the study. The reader is referred to a companion report (Heberlein et al., 2017a) for a full description of the Lara results.

At Mount Washington, the sample media and methods used are similar to those employed at the Lara study site (Heberlein et al., 2017a). However, to assist in understanding dispersion processes, a key component of this study is the use of ion-collection devices, or traps, consisting of activated charcoal and alkaline ion-exchange resin packages that were buried in the soil profile for three months in an attempt to capture volatile anions and cations emanating from the ground. Furthermore, the flux of these components through vegetation is measured through the analysis of transpired fluids exuded from mountain hemlock (*Tsuga mertensiana*) needles, and in snow. Snow analysis should provide a measurement of volatiles emanating from the ground.

Objectives of this study are:

- a) To broaden the range of sample media tested for halogens and other volatile components to include, in addition to the dominant conifer species: transpired fluid, passive ion collectors and snow.
- b) To evaluate halogen and other volatile component responses over known epithermal style mineralization and to compare them to background areas.
- c) To develop and optimize analytical methods for low level detection of halogens in organic-rich samples.
- d) To develop a model for the cycling of halogens between the ground, vegetation and snow.

## ***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 in organic sample media and soils. It provides exploration companies with knowledge and guidelines about the best media to sample as well as advice on the appropriate sample digestion and analytical methods to use. The study also provides knowledge of the geochemical patterns that can be expected in different geological

and cover situations as well as an understanding of how the volatile components disperse in the near surface environment.

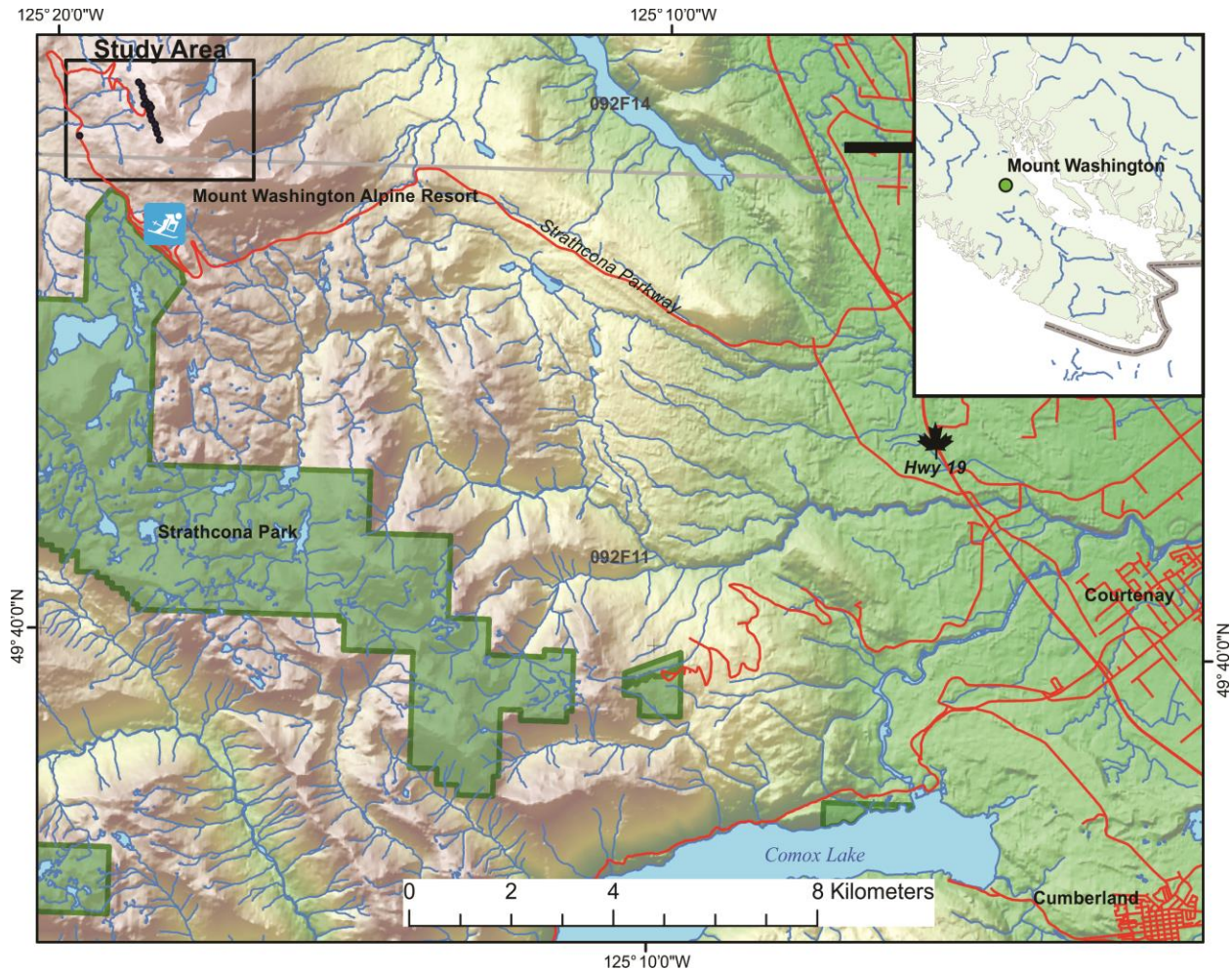
## **Study Area**

The Mount Washington epithermal Au prospect is located near the city of Courtenay on Vancouver Island. A biogeochemical study of the area, conducted by the Geological Survey of Canada in 1990, revealed strong geochemical signals of the commodity and pathfinder elements related to the underlying mineralization (Dunn, 1995, 2007). This indicated that Mount Washington would be a suitable area for testing the volatile components sought in this study. Furthermore, archived samples from the 1990 survey were available for additional analysis.

At Mount Washington, the sampling approach was somewhat different from that at Lara. In addition to collecting plants and soils to assess their volatile-compound concentrations and spatial patterns around the mineralized zone, artificial media were placed in the ground to collect ions that may be migrating to the surface from the underlying rocks. By using this novel approach, the aim is to establish if there is, indeed, a vertical flux of volatile compounds emanating from the bedrock. Activated carbon and alkaline ion-exchange resin were used as collectors for these mobile cations and anions. Results from the artificial media are compared to patterns in natural media, including Ah horizon soil, vegetation (mountain hemlock and Yellow-cedar) and transpired fluids collected from the dominant species (mountain hemlock).

## **Location and Access**

The study area lies immediately north of the Mount Washington Alpine Resort (Fig. 1). Access from the nearest logistical centre at Courtenay is via Highway 19 north to the Strathcona Parkway and then west for 10 km to the alpine resort, all on well-maintained paved roads. From the alpine lodge, the sampling area is accessible on foot via mountain biking trails and ski runs to the Boomerang chair lift and then by a network of old drilling and mining roads to the northwest. Alternative access can be gained by four-wheel-drive vehicle from the Raven Lodge parking area via a network of variably maintained logging and mining roads and trails (Fig. 1).



**Figure 1:** Location of the Mount Washington study area (black box), east-central Vancouver Island. Sample locations indicated by black dots.

## Surficial Environment

The sampling area lies at mid-slope (approximately 1360 m elevation) on the western flank of Mount Washington, just above the transition between steeper colluvial slopes above and gentler, poorly drained slopes below. Drainage development at the sampling elevation is poor.

Much of the area has been previously logged. Present-day vegetation consists of open subalpine woodland containing a variety of tree species, including: Yellow-cedar (*Chamaecyparis nootkatensis*), mountain hemlock (*Tsuga mertensiana*), Pacific silver fir (or Amabilis fir; *Abies amabilis*) and subalpine fir (*Abies lasiocarpa*). The dominant understory species is white-flowered rhododendron (*Rhododendron albiflorum*).

Surficial geology is relatively simple. Above about 1320 m, the hillsides are covered with a veneer of colluvium. Exposures in roadcuts show that this material rarely exceeds 2 m in thickness and, over much of the sampled area, it is less than 0.5 m thick. A thin soil profile is developed on this sandy matrix material. Observations from sample holes and roadcuts show that the most common profile consists of poorly developed eutric Brunisols and ferric podzols, typified by a surface LFH layer and a thin Ah horizon (<2 cm) overlying a uniform, brown,

undifferentiated Bm horizon. Incipient podzolization, marked by the presence of an intermittent eluvial Ae<sub>j</sub> horizon and Bf or Bh horizons, is present at about 10% of the sample locations (Fig. 2).



**Figure 2:** A typical ferric podzol soil profile from the central part of the sample traverse.

Below the 1320 m contour, particularly in the northwest corner of the survey area, there is an abrupt transition from well-drained colluvium to water-saturated ground. This elevation is marked by an almost continuous line of meltwater-fed springs and seeps that form a series of small raised bogs that feed downslope into small ponds and lakes. These water bodies define the headwaters of streams that drain the slope westward into the northwest-flowing Goss Creek

## Geology

This study was carried out over the western part of the Lakeview-Domineer resource area (Houle, 2013), which comprises several shallow-dipping Au-Ag-Cu-bearing quartz-sulphide veins and steeply dipping breccia bodies (Fig. 3).

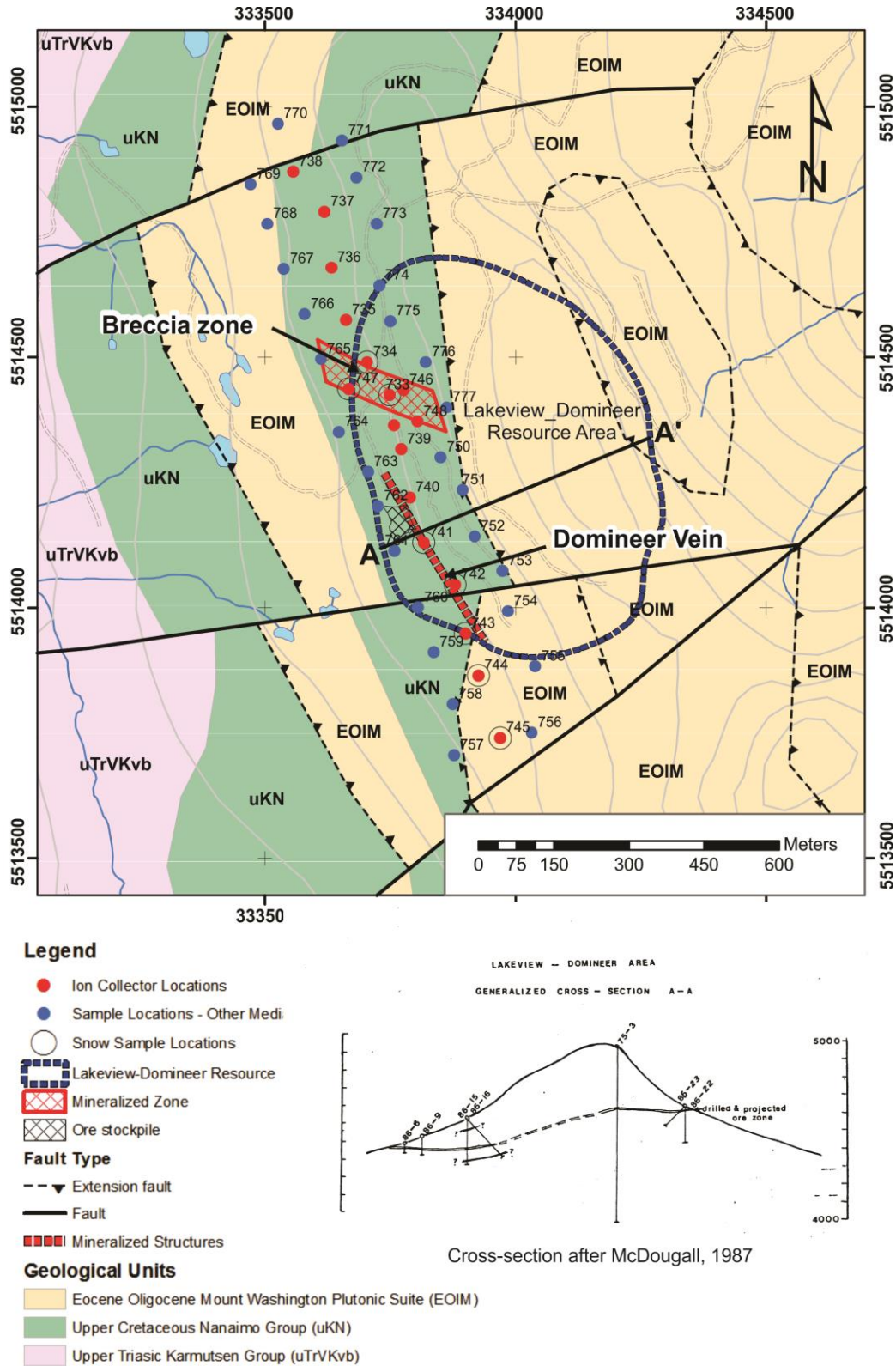
The Lakeview-Domineer zone (MINFILE # 092F116) has been exploited in two small open pits and explored by extensive diamond-drilling, trenching, bulk sampling and underground drifts. Production by Mount Washington Copper Co. Ltd. between 1964 and 1967 was 381,733 tonnes grading 0.34 g/t Au, 19 g/t Ag and 0.93% Cu (Houle, 2013, 2014).

From the most up-to-date geological mapping of the Mount Washington area (Massey et al., 2005 after Muller, 1988), it is apparent that most of the study area on the west slope of Mount Washington is underlain by pillow basalts of the Triassic Karmutsen Formation. On the upper slopes, the basalts are unconformably overlain by a gently east-dipping sequence of sandstone, siltstone and conglomerate of the Upper Cretaceous Nanaimo Group. This is the main unit underlying the sampled area. The ridges and upper elevations of the mountain are underlain by intrusive rocks, consisting of quartz diorite and feldspar-hornblende dacite porphyries that

together make up the Eocene–Oligocene (41–35.5 Ma; Madsen et al., 2001) Mount Washington Plutonic Suite. The intrusions occur as stocks, sills and dike-like bodies that intrude the Nanaimo Group sediments

At least seven different breccia bodies, some pipe-like and others more flat-lying, have been recognized in the Lakeview-Domineer resource area (Houle, 2013). Zones of brecciation are localized along the intrusive contacts and on north and northeast and northwest-trending structures. They vary widely in texture and composition, and appear to be the principal controls for sulphide mineralization. Mineralization also occurs in veins and stringers. The style of mineralization is high sulphidation epithermal Au-Ag-Cu (BC Mineral Deposit Profiles L01, H04; Panteleyev, 1995) or ‘subvolcanic’ Cu-Au-Ag style (L04; Panteleyev, 1995; Houle, 2013).

Two mineralized bodies are present at the study location: one consists of a ESE trending breccia body (referred to hereafter as the ‘breccia zone’) exposed on drill roads in the middle of the area; and the second is a flat-lying vein breccia known as the Domineer vein whose surface trace follows the contour on the slope in the south-central part of the sampled area. The breccia vein is exposed in the (now collapsed) portal of the Domineer adit. The extents and precise geometries of these zones are not well constrained and the shapes of the mineralized zones and their positions shown in Figure 3 are our best approximations based on field observations and historical information (McDougall, 1987; Houle, 2014).



**Figure 3:** Geology map of the Mount Washington study area (after Murray, 1988) with sample locations.

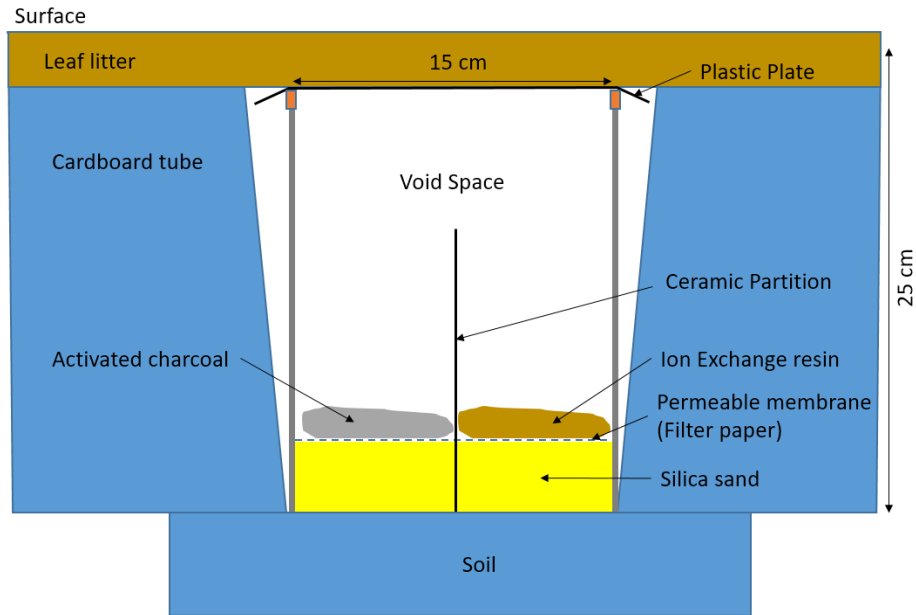
## Sampling

The Mount Washington sampling campaign was divided into three parts. Part 1, carried out 27-30<sup>th</sup> June, involved the installation of 18 passive ion collectors along a south-southeast-trending traverse over the Domineer Au zone (Fig. 3) and the collection of foliage and transpired fluids from mountain hemlock at the same sample stations. Ion collectors were installed at nominal 100 m intervals. A single collector was also installed in a similar setting at a presumed unmineralized area located 1500 m to the west, to act as a background control site. A summary of samples collected is presented in Table 1.

**Table 1:** Numbers and types of samples collected for the Mount Washington study.

Sample medium	No. Samples	No. Duplicates	No. Controls	Comment
Mountain hemlock foliage (MHF)	73	5	2 (V14)	Collected June, 2016
Ion collectors (IC)	19	2		Put in place, June 2016; recovered October, 2016.
Transpired fluids (TFMH)	18	2		Collected August, 2016
Ah horizon soils	39	4	4 (LIM-2011)	Collected October, 2016
Snow	18	2		Collected April, 2017
Archived yellow cedar bark ash (YCB)	17			Collected August 1990

The ion collectors contained two different collection media: activated charcoal for cations and alkali ion-exchange resin for anions (Sigma Aldrich Amberlite IRA743<sup>®</sup>). The media were accurately weighed into 10 by 7 cm porous nylon sachets (15 and 20 g, respectively) that were then heat sealed. In the field, they were placed on a 2 cm bed of pure silica sand housed in an 18 cm diameter by 15cm deep cardboard tube that was buried to 20 cm (Fig. 4). The silica sand served to isolate the collectors from the soil to avoid capture of endogenic ions: a filter paper was used to isolate the collectors from the silica sand and a ceramic tile was placed between the collectors to avoid the possibility of cross-contamination between the charcoal and resin sachets. The apparatus was capped with an overlapping plastic plate to prevent entry of rain water and surface debris, and the device was shallowly buried. Each site was sprayed with animal repellent to discourage disturbance by curious bears. An example of a partially installed collector is illustrated in Figure 4 (bottom). Duplicate collectors were buried at two of the sites: one over mineralization and the other at a background location. The ion collectors were left in the ground for three months.



**Figure 4:** Top – Ion collector device design. Bottom - an example of a partly installed collector.

In addition to installing the passive collectors, mountain hemlock (*Tsuga mertensiana*) foliage (MHF) and transpired-fluid samples were collected at each location. Transpired fluids (from mountain hemlock) were obtained by enclosing several 25 cm lengths of twig with needles in plastic bags and leaving them for a minimum of 24 hours during a period of sunny weather (Fig. 5 - left). After that time, the transpired fluid was recovered by removing the bags and taking up the fluid in a 60 mL syringe (Fig. 5 – right). A 0.45  $\mu\text{m}$  filter was then attached to the end of the syringe and the liquid filtered into 25 mL glass vials. The glass vials were placed in a cooler with ice packs for transportation to ALS Minerals in North Vancouver.

Mountain hemlock foliage was collected from around the circumference of a single tree at each sample site by snipping off approximately 25 cm lengths of twig (representing 7 years of growth) from chest height. Foliage samples were placed in porous Hubco Sentry II fabric sample bags.



**Figure 5:** Collection of transpired fluid (left) and filtration of fluid into glass vial (right).

Part 2 of the sampling program, carried out on October 4<sup>th</sup> and 5<sup>th</sup>, involved recovery of the ion collectors and collection of Ah horizon soil and additional MHF samples.

Ion collectors were carefully recovered and each medium placed in separate Ziploc<sup>®</sup> bags. Both bags were then placed in a third bag to isolate the samples from the atmosphere. All the used materials were removed from the sample sites and disposed of and the sample holes filled.

Additional vegetation samples included repeats of the Part 1 sites as well as collection of samples from parallel sample lines 100 m to the east and west of the ion-collector line.

## **Snow Sampling**

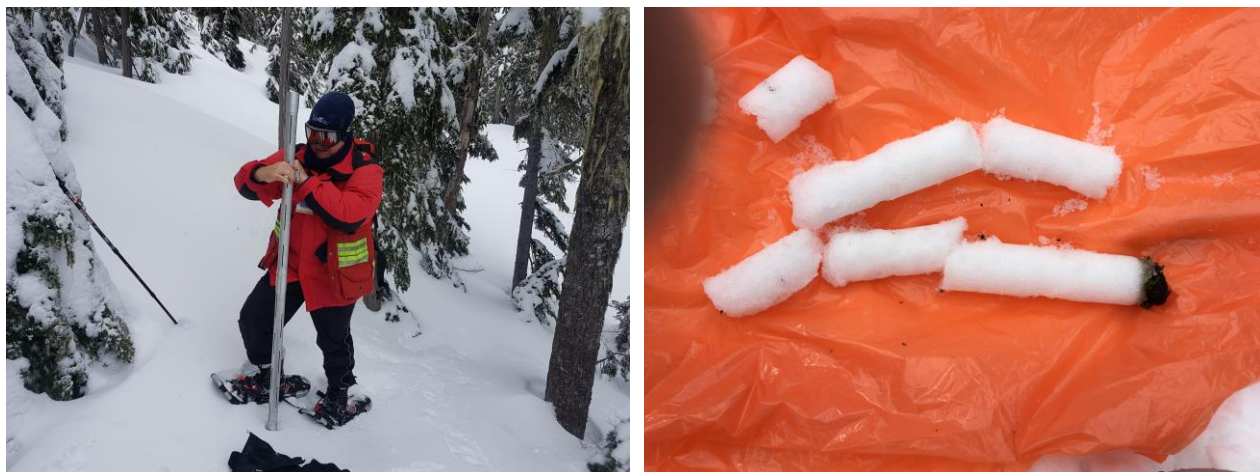
The third and final part of the sampling program, involving the collection of snow samples, was completed in early April 2017. A record snow pack, averaging 3-4 m at the sampling sites, and avalanche hazard meant that only eight of the ion collector sites could be safely sampled: three over the breccia zone four over the Domineer trend and one at a background site (Fig. 3).

Sampling was done with a Federal snow sampler tube. At each site the sampling tube was screwed into the snow pack until it reached the ground surface (Fig. 6 - left). A plug of the frozen soil was collected to establish that the ground surface had been reached (Fig. 6 – right). The snow core for the lower 50 cm of the snow pack was then removed from the tube and placed on a plastic sheet (Fig. 6). The soil plug was removed and the 10 cm of the snow core

immediately above it was placed into a wide-mouth HDPE plastic container. Three cores were necessary at each site to ensure that sufficient liquid ( $>60$  ml) was obtained on melting.

In addition to the base of snow, samples from the mid-depth and surface were collected at two of the sites (locations 734 and 745; Fig. 2). Duplicates were collected from two sample stations (734 and 743).

Table 2 summarizes the sampling depths and QC samples for each sampled site.



**Figure 6:** Left - Sampling with the Federal snow sampler. Right - core from the lower 50 cm of the snow pack with the soil plug at the end.

**Table 2:** Summary of snow samples and snow pack depths.

Sample Site	Depth (cm)	QC
733	305	
734	0	Duplicate
734	130	Duplicate
734	265	Duplicate
740	325	
741	315	
742	285	
743	287	Duplicate
744	335	
745	0	
745	190	
745	383	
747	230	

## Analytical Methods

### General

Whereas the scientific literature contains many papers dealing with the analysis of volatile elements, most of these involve time-consuming and expensive methods that are beyond the reach of most exploration budgets; therefore, they tend not to be offered by mainstream commercial laboratories. Most commercial laboratories offer F analysis of inorganic samples by Ion Selective Electrode (ISE) after either a KOH or Na<sub>2</sub>O<sub>2</sub> 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 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 in solvent-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 ion chromatography on a KOH fusion; detection limits that are again too high to be of practical use for some surficial sample media. Pyrohydrolysis coupled to IC is the standard for F and Cl determinations on samples with significant organic content, but it is not widely available outside coal-focused laboratories who have not developed trace level methods for the instrument.

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 achieve detection limits of 0.001 ppm for I on their water leach-ICP-MS method.

Kaveh et al. (2017) demonstrated the effectiveness of electro-thermal volatilization-ICP-MS (ETV-ICPMS) as a means of analyzing Cl, Br and I to a 0.01 ppm detection limit. This method avoids the necessity of a chemical digestion and potential organic interferences by volatilizing the solid sample into an argon stream for direct introduction into the plasma. While this method shows great promise for organic-rich samples, it is not widely available at commercial laboratories.

The main challenge for this project is defining a method of analyzing the halogens and anions to geologically meaningful detection limits while dealing with the interferences caused by high organic contents of the chosen sample media. Identification of an effective analytical method involved a significant amount of research that was carried out at the BC Ministry of Environment (BCMOE) in Victoria, BC and at ALS Minerals Ltd. in North Vancouver. Details of the development of the analytical methods are summarized below.

## Halogen and Anion Method Development

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

Initial experimentation was done with HPLC-IC on a warm water leach of 0.5g aliquots of powdered western hemlock needles (WHF) in accord with the method developed by Hall under Geoscience BC Project 2005-008 (Dunn et al., 2007). The vegetation samples used for the initial studies were collected from the Lara project area (Heberlein and Dunn, 2017a; Heberlein et al., 2017a).

Leachates from approximately 200 vegetation samples from Lara (Heberlein et al., 2017a) and Mount Washington were analyzed by HPLC-IC for Cl, Br, I, NO<sub>2</sub>, NO<sub>3</sub>, NH<sub>4</sub>, PO<sub>4</sub> and SO<sub>4</sub> at the BC Ministry of Environment laboratory in Victoria, BC. The solutions were analyzed on an auto analyzer (an automated analyzer using continuous flow analysis (CFA)), for nitrate-nitrite (NO<sub>2</sub>+NO<sub>3</sub>) and ammonium (NH<sub>4</sub>). Chlorine, Br and I were determined by ion chromatography; F was determined separately by ISE. From the control sample results, it was evident that the first batch of HPLC-IC results exhibited considerable variability in analyte concentrations, indicating that the accuracy and precision of the method was poor and it was concluded that this approach would not achieve the desired results.

Extensive research was subsequently undertaken to refine the methodology. After several iterations of the analyses, the laboratory concluded that the HPLC-IC method was too imprecise and the detection limits too high to achieve meaningful results. The following is an excerpt from the laboratory's internal report on the HPLC-IC experimentation describing the difficulties encountered (Sadowy, 2016, pers. comm.):

*Finely ground vegetation samples were incubated at 30°C for 1 hour (2 g in 20 mL 18 mohm H<sub>2</sub>O). The 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 instead of larger batches.*

*These water leachates were then analyzed using a Waters 1525 HPLC pump outfitted with a Metrohm ion suppressor and detection by conductivity (for Cl, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) and UV (for Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and I<sup>-</sup>). To begin with, the analysis used a Grace Novosep A-2 anion column (5µm, 250 x 4mm). The samples proved to be very hard on the column because of the large amounts of organic compounds 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<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> and low levels of Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and I<sup>-</sup>. The high dissolved organic concentration caused degradation of the column's ability to resolve peaks over time; therefore, a new column was used to finish the analysis (Shodex SI-524E™, 5 µm, 250 x 4mm). This column proved to have much better resolution than the previous one. However, over time, with the difficult sample matrices, 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  $\text{Cl}$  and  $\text{PO}_4^{3-}$ ) if a single peak was the anion overlapping with unknown peaks, 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.  *$\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{I}^-$  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  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{I}^-$  were somewhat doubtful.*
6.  *$\text{F}^-$  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 as an alternative means to measure  $\text{F}^-$  if the concentrations are  $>0.1\text{ppm}$ .*
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  $30^\circ\text{C}$  is not much different from 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  $30^\circ\text{C}$ .*

*Given these constraints and difficulties outlined above, the laboratory concluded that while reasonably low detection limits could be achieved (Table 3), lack of precision of the method was a significant problem and rendered many of the analyte results unusable. Furthermore, the time and cost involved with the HPLC-IC method renders the technique impractical for exploration applications if organic rich sample media are to be analyzed.*

**Table 3:** Detection limits obtained by the BC Ministry of Environment laboratory after optimizing the methodology.

HPLC Analyte	Detection Limit (ppm)	Detection Method
Br <sup>-</sup>	0.65	Ultra-violet
I <sup>-</sup>	0.65	Ultra-violet
NO <sub>2</sub> <sup>-</sup>	0.40	Ultra-violet
NO <sub>3</sub> <sup>-</sup>	0.40	Ultra-violet
Cl <sup>-</sup>	0.65	Conductivity
PO <sub>4</sub> <sup>3-</sup>	2.00	Conductivity
SO <sub>4</sub> <sup>2-</sup>	1.00	Conductivity

### Determination of F and Cl by IC.

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 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 ammonium to remove the formed nitrate, it proved impossible to isolate the F peak from the broader interfering nitrate peak.
- 2) Use of ultrapure H<sub>2</sub>O<sub>2</sub> to leach samples. The F peak could not be resolved from the chromatograms due to interference with a strong overlapping OH<sup>-</sup> response.
- 3) Ashing – A suite of mountain hemlock foliage from Mt. Washington and sword fern foliage from the Lara area (Heberlein et al., 2017a), 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 oven. The LOI oven method was initially pursued to reduce the time required for ashing to keep the cost of a final method low. Samples were initially 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, 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 by ME-HAL01a 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
<b>mean</b>	<b>18.4</b>	<b>1318.8</b>	<b>7.69</b>	<b>1235.3</b>	-	<b>1419.3</b>
<b>%RSD</b>	<b>5</b>	<b>1.59</b>	<b>115.4</b>	<b>6.7</b>	-	<b>12.7</b>
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
<b>mean</b>	<b>5.4</b>	<b>1005.8</b>	<b>2.95</b>	<b>900.7</b>	-	<b>1016.5</b>
<b>%RSD</b>	<b>6.5</b>	<b>1.54</b>	<b>116.1</b>	<b>6.3</b>	-	<b>7.3</b>
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
<b>mean</b>	<b>17.7</b>	<b>578.3</b>	<b>14.24</b>	<b>468.7</b>	-	<b>745.7</b>
<b>%RSD</b>	<b>10.6</b>	<b>4.07</b>	<b>66.73</b>	<b>1.3</b>	-	<b>3.7</b>

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, and was used for analysis of the MHF, Ah horizon and charcoal ion collectors.

### ***Other analytical methods***

In addition to the approaches discussed above, several other analytical methods were tested on the Ah horizon soil samples, charcoal and resin ion collectors, and vegetation samples. A summary of analytical methods used is presented in Table 5.

Ah horizon samples were oven dried at 80°C and sieved to -80 mesh (<177 µm). A 0.5g aliquot of the fine fraction was then decomposed with a modified aqua regia digestion and analyzed for 53 elements by the ME-MS41L method. Milled MHF samples were ashed at 485 °C for 16 hours (method VEG-ASH01); a 0.5g aliquot was digested with aqua regia and analyzed by ICP-MS

(method ME-VEG41a). Another 0.5g aliquot was leached with warm water and analyzed for F, Cl, Br and I by IC and ICP-MS (ALS method ME-HAL01a.)

Splits of the Ah horizon soil and milled MHF were shipped to Actlabs in Ancaster Ontario for analysis by their proprietary Bioleach method. A 0.75 g sample is partially digested in a proprietary matrix weak leach at 30° C for 1 hour, and the solutions are analyzed on a Perkin Elmer ELAN 6000, 6100 or 9000 ICP/MS. Bioleach has proved to be effective for determination of the halogens Br and I in organic-rich samples to very low levels.

Melted snow samples were analyzed directly for Cl, Br and I by ICP-MS. Initial results showed that concentrations of Br and I were too low to be detectable. To increase the concentrations to detectable levels, the solutions were pre-concentrated by evaporating them down to 20% of their original volume on a hot plate at 100 °C. Iodine was stabilized in solution by spiking with 5% NH<sub>4</sub>OH. Analytical results from the concentrated solutions did provide detectable concentrations as discussed in the results section.

The transpired fluids and snow samples were analyzed directly for multi-elements by ICP-MS (ALS method ME-MS14L) and by IC/ICP-MS (ALS method ME-HAL01w) for the halogens.

Sample Medium	Laboratory	Digestion	Analytical Method	Analytes
MHF <sup>1</sup>	BC MOE Laboratory, Victoria, BC	H <sub>2</sub> O leach; 30°C for 60 minutes	HPLC-IC <sup>2</sup>	NH <sub>4</sub>
MHF	ALS Minerals, N. Vancouver, BC	VEG-ASH01 <sup>11</sup> ; ME-HAL01a; ME-MS03.	IC/ICP-MS	F, Cl, Br, I
		ME-VEG41L <sup>4</sup>	ICP-MS	Multi-elements including Br and I
MHF	Actlabs	Bioleach <sup>6</sup>	ICP-MS	Multi-elements including Br and I
YCB <sup>1</sup>	ALS Minerals, N. Vancouver, BC	ME-HAL01a <sup>3</sup> , ME-VEG41L	IC/ICP-MS	F, Cl, Br, I
		HAL-PREP01 <sup>12</sup> , ME-HAL01	ICP-MS	Multi-elements including Br and I
Ah Horizon soil	ALS Minerals, N. Vancouver, BC	ME-MS41L	IC/ICP-MS	F, Cl, Br, I
		LOI <sup>5</sup>	ICP-MS	Multi-elements, including Br and I
	Actlabs	Bioleach		
Transpired Fluids	ALS Minerals, N. Vancouver, BC	None	IC	F, Cl
		ME-MS14L <sup>7</sup>	ICP-MS	Multi-element including Br and I
Snow	ALS Minerals, N. Vancouver, BC	None	IC/ICP-MS	F, Cl, Br, I
Charcoal Ion Collector	ALS Minerals, N. Vancouver, BC	VEG-ASH01 <sup>10</sup> , ME-HAL01a.	IC/ICP-MS	F, Cl, Br, I
		ME-MS07 <sup>8</sup>	ICP-MS	Multi-element including Br and I
Resin Ion Collector	ALS Minerals, N. Vancouver, BC	ME-MS05, ME-MS03	ICP-MS	Multi-element including Br and I

<sup>1</sup> MHF - Mountain hemlock foliage; YCB - Yellow cedar bark

<sup>2</sup> HPLC-IC - High Performance Liquid Chromatography and Ion Chromatography

<sup>3</sup> ME-HAL01 - HAL-PREP01 preparation; ME-HAL01a - VEG-ASH01 preparation. Both with de-ionized H<sub>2</sub>O leach and ICP-MS/IC finish for halogens

<sup>4</sup> ME-VEG41L - Modified aqua regia digestion; super trace ICP-MS finish.

<sup>5</sup> Loss on ignition - 485° for 180 minutes.

<sup>6</sup> Bioleach - Actlabs proprietary method.

<sup>7</sup> ME-MS14L - Super trace analysis of natural waters

<sup>8</sup> ME-MS07 - Sodium pyrophosphate leach

<sup>9</sup> ME-MS05 - Cold hydroxylamine hydrochloride leach

<sup>10</sup> ME-MS03 - Warm water leach

<sup>11</sup> VEG-ASH01 - Milled vegetation ashed at 485 ° for 16 hours

<sup>12</sup> HAL-PREP01 - Ashing at 485° for 90 minutes (soils and sediments).

**Table 5:** Summary of analytical methods.

Analysis of the ion collectors was carried out using three different methods. Charcoal collectors were ashed for 16 hours at 485°C and analyzed for the halogens by ME-HAL01a. A 1.0 g split was also analyzed by ICP-MS after leaching with 25 mL of sodium pyrophosphate solution, rolling for 60 minutes at room temperature and then centrifuging to remove solids.

Halogen analysis of the resin collectors could not be undertaken with the ME-HAL01 method. The medium was found to completely vapourize at 485°C, leaving no material for analysis. A 1.0 g sample of resin was leached with a weak acid leach (cold hydroxylamine hydrochloride – ALS method ME-MS05) and multi-element analysis by ICP-MS. Chlorine, Br and I were analysed by ICP-MS after a warm water leach. Results for most elements including Br and I were below detection limit.

## Quality Control

Quality control measures employed at Mount Washington include the collection of field duplicate samples for each sample type as well as the insertion of control samples. For the vegetation, the control material was milled mountain hemlock needles from Mt. Washington (control V14) that had been collected and characterised more than a decade earlier. For the Ah horizon, a bulk Ah standard sample from Ireland (LIM-2011) was provided by Steve Cook from Teck Resource Limited. This material has been certified by round robin analysis involving six internationally accredited laboratories.

## 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):

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

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) when 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 8 summarizes the average coefficients of variation (%CV) for the different analytical methods and sample media. The overall precision for the halogens is not very good with some of the media having coefficients of variation of well over 50%. Of note are the high %CV's for the transpired fluids. Values of >70% can be partly attributed to the small duplicate sample population (2) and very low concentrations but large differences in halogen concentrations in fluids from adjacent trees is surprising. Precision for the snow analyses is somewhat better than

for the transpired fluids but is still at an unacceptable level of over 50%. Poor precision in fluid samples is unlikely to be caused by analytical error; the laboratory's internal duplicates sample repeat very well (see certificate of analysis in Appendix A). The cause for the poor precision in the fluid duplicates is not well understood.

**Table 6:** Summary of average coefficients of variation for field duplicate results.

Analyte	Method	Bioleach		ME-HAL01a <sup>1</sup>			ME-HAL01 <sup>2</sup>	ME-MS03 <sup>3</sup>	ME-MS14L <sup>4</sup>		MW Digestion <sup>5</sup>	ME-MS07 <sup>6</sup>
			MHF	YCB_Ash	MHF	Ion Collector Charcoal	Ah Soil	MHF	Transpired Fluids	Snow	MHF	Ion Collector Charcoal
F	IC	-	-	-	BDL	16.86%	98.61%	-	72.98%		19.71%	-
Cl	IC	-	-	-	-	25.06%	61.66%	-	79.07%		-	-
Cl	ICP-MS	-	-	-	33.96%		-	-		54.06%	36.95%	-
Br	ICP-MS	50.63%	57.60%	-	15.54%	13.84%	61.72%	-	78.85%	58.71%	19.67%	14.17%
I	ICP-MS	48.07%	11.00%	-	32.08%	34.91%	33.25%	-	84.09%	53.72%	33.46%	BDL
NH <sub>4</sub>	-	-	-	-	-		-	20.84%	-		-	-
PO <sub>4</sub>	-	-	-	-	-		-	24.64%	-		-	-
SO <sub>4</sub>	-	-	-	-	-		-	76.11%	-		-	-

<sup>1</sup> ME-HAL01a - Ashed at 485°C for 16 Hours; Warm de-ionised water leach with ICP-MS/IC finish for the halogen elements (vegetation).

<sup>2</sup> ME-HAL01 - Ashing at 485°C for 90 minutes; Warm deionised water leach and ICP-MS/IC finish for halogen elements (soils).

<sup>3</sup> ME-MS03 - Warm water leach of milled foliage.

<sup>4</sup> ME-MS14L - Water analysis by ICP-MS.

<sup>5</sup> 10% HNO<sub>3</sub> microwave digestion.

<sup>6</sup> Sodium pyrophosphate leach.

Unacceptably high values are also observed in the Ah horizon ME-HAL01 results where the %CV for F and Cl by IC are well over 50%. In fact, for F the value of 98.61% suggests that the results may be of little value in revealing geologically relevant patterns. Ah horizon field duplicates for the Bioleach are also at the usable limit. The fact that this medium's precision is consistently poor across several methods may say something about the way the halogens are distributed in the Ah horizon. It appears that they are not uniformly distributed and may be concentrated in material with erratic distribution in the soil, such as organic matter. This is investigated further in the discussion section.

Mountain hemlock foliage duplicates have generally better %CV values than the other media, perhaps reflecting the more homogeneous nature of this sample type. For the ME-HAL01 method, Cl, Br and I all have %CV's below 35%. Acceptable values are also achieved by the microwave digestion, which produced values ranging from a high of 36.95% for Cl (by ICP-MS) to a low of 19.67% for Br. In Bioleach, I has a very good precision of 11.00% but Br is less consistent between the duplicate samples with a %CV value of 57.60%.

The charcoal ion collectors have the best reproducibility of all media. For ME-HAL01 the %CV's vary between 34.91% for I and 13.84% for Br. This method also achieves the best precision for F (16.86%). A similar %CV is achieved for Br (14.17%) in the sodium pyrophosphate leach; I values are below detection limit for this method.

For the anions determined by HPLC-IC on MHF, NH<sub>4</sub> and PO<sub>4</sub> have acceptable precisions of 20.84% and 24.64% respectively, while SO<sub>4</sub> has an unacceptable precision of 76.11%.

## Accuracy

Control samples were used for Ah horizon (LIM-2011) and vegetation (V14) analyses, but neither is certified for halogens or the analytical methods employed. Hence, they cannot be used to monitor the absolute accuracy of the analytical results. Instead, the control results may be used as 'drift monitors' to identify systematic errors in the data as well as to estimate the precision of the analytical methods.

Table 7 shows the percent relative standard deviations (RSD) results for each standard across the range of analytical methods. It should be noted that Ah horizon ME-HAL01 analyses were carried out without the LIM-2011 controls.

For the Bioleach results on control LIM-2011, I precision is very good (5.58%), however, Br precision is disappointing (27.64%). The reason for the degraded Br precision can be attributed to one poor analysis with a reported value of almost 60% higher than the mean concentration of the other four analyses (sample Ah-734C – 8130 ppb vs. mean – 5063 ppb). If this analysis is removed from the RSD calculation, the remaining four determinations show more respectable RSD of 17.37%.

Bioleach V14 results show much the same pattern as the LIM-2011 results with Br having a relatively high RSD of 18.76% caused by a single outlier analysis. If the high value is excluded from the RSD calculation, the remaining three controls yield a more acceptable average RSD of 12.99%.

For the ME-HAL01 method, precisions for the IC analyzed elements F and Cl are good (2.26% and 9.36% respectively). Bromine and I determined by ICP-MS have marginally acceptable precisions of 21.55% and 17.14%. The reason for the poor precision in the ICP-MS analyses is unclear.

**Table 7:** Percent relative standard deviations for control samples.

LIM-2011						
	Medium	N	F	Cl	Br	I
Bioleach	Ah Soil	5	na <sup>1</sup>	na	27.64%	5.58%
HAL-01	Ah Soil	0	na	na	na	na

V14						
	Medium	N	F	Cl	Br	I
Bioleach	MHF	4	nr	nr	18.76%	4.80%
HAL-01	MHF	5	2.26%	9.36%	21.55%	17.14%

<sup>1</sup> - Not analyzed

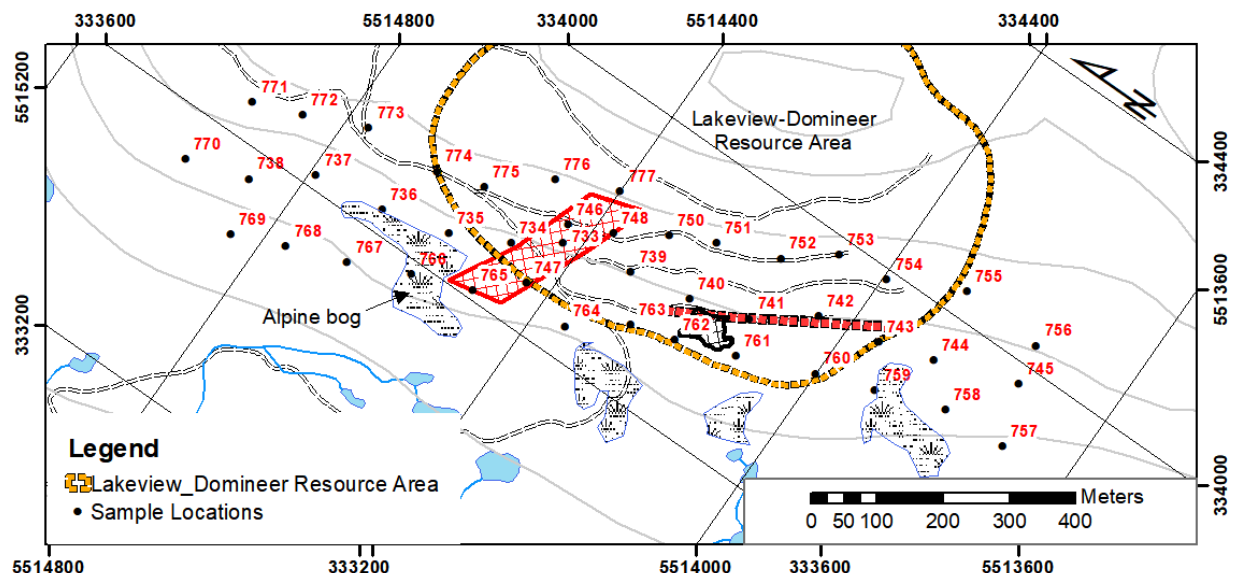
## Results

In this section, the halogen results for the different sample media are described. They are presented as scaled symbol plots superimposed on a topographic base map with the position of the observed mineralization highlighted for reference (red cross-hatching). Additionally, the locations of a bulk sample dump (black hatching), outside the entrance to the Domineer adit, and several alpine bogs are shown to aid with the interpretation of the results.

Results are described from the ground up, starting with Ah horizon soils and ion collectors and progressing through the vegetation sample and ending with the transpired fluids and snow. In other words, following the assumed pathway of halogen flux from the ground upwards.

Figure 7 shows the locations of the sample sites. Note that the map orientation is rotated to more efficiently fit it on a page. It should also be noted that complete suites of sample media were not collected at each sample location. Descriptions of the results for each medium include a sample location map showing where a sample type was collected.

Sampling was done along three WNW-ESE traverses approximately 100 metres apart, across the Lakeview-Domineer resource area (LDRA – Houle, 2014). LDRA, shown by the red polygon in Figure 3 and yellow polygons on the following figures, is the approximate plan envelope of the Lakeview-Domineer mineralized system as defined from historical drill holes (Houle, 2013, 2014). It is not continuously mineralized at the surface as demonstrated by the presence of unaltered and unmineralized outcrops on old drill roads and in incised drainages at various positions on the sample traverses. Observed mineralization is limited to the area indicated by the red hatching on Figure 7. Unfortunately, no accurate or complete maps showing the exact positions of the mineralized bodies are available.



**Figure 7:** Sample locations referred to in the discussion of results. Red hatching – observed mineralization, black hatching – dump of mineralized material at Domineer adit portal. Domineer vein shown as dotted red line.

## Summary Statistics

Summary statistics for the halogens results for each medium are presented in Table 8.

**Table 8:** Summary Statistics for Halogens.

	F ppm								
	Ah	CC	Ah_Bio	MHF-Bio	MHF	RC	TF	Snow	YCB
Count Numeric	32	16			14		15		17
Minimum	0.05	1.05			0.05		0.272		391
Maximum	20.9	6.76			3.39		3.974		1245
Mean	6.1	1.9			0.4		1.1		714.5
Median	6.03	1.39			0.025		0.56		639
Standard Deviation	5.9	1.4			1.1		1.1		232.4

	Cl ppm								
	Ah	CC	Ah_Bio	MHF-Bio	MHF	RC	TF	Snow	YCB
Count Numeric	32	16			14	18	13	9	17
Minimum	14.4	630			712	98.5	0.201	4.95	0.05
Maximum	3380	2820			3140	210.18	7.396	13.19	446
Mean	471.1	1555.9			1779.1	142.1	2.1	7.5	59.5
Median	200.0	1300.0			1725.0	139.8	1.1	7.1	0.1
Standard Deviation	724.1	667.4			650.8	31.3	2.4	2.5	110.8

	Br_ppm								
	Ah	CC	Ah_Bio	MHF-Bio	MHF	RC	TF <sup>1</sup>	Snow <sup>1,2</sup>	YCB
Count Numeric	32	16	33	45	14	18	15	9	17
Minimum	0.91	43.5	127	0.128	14	0.006	0.005	20	1.06
Maximum	271	923	1520	3.99	59.9	0.078	0.032	64	24.3
Mean	24.6	211.0	437.2	0.6	36.0	0.0	0.0	14.0	9.9
Median	7.415	149.5	346	0.356	36.8	0.0065	0.012	58	9.14
Standard Deviation	50.9	226.4	315.4	0.7	13.4	0.0	0.0	17.0	6.4

	I ppm								
	Ah	CC	Ah_Bio	MHF-Bio	MHF	RC	TF	Snow <sup>1,2</sup>	YCB
Count Numeric	32	16	33	45	14	18	15	1.7	17
Minimum	0.013	0.043	23	0.015	0.296	0.001	0.001	1.7	0.052
Maximum	4.55	0.329	271	0.047	0.957	0.007	0.005	31.3	0.196
Mean	0.370	0.146	94.940	0.026	0.551	0.003	0.003	6.8	0.116
Median	0.069	0.1235	75	0.026	0.5545	0.002	0.003	29.6	0.12
Standard Deviation	0.876	0.082	61.980	0.006	0.187	0.001	0.001	9.30	0.047

1 - Liquid sample

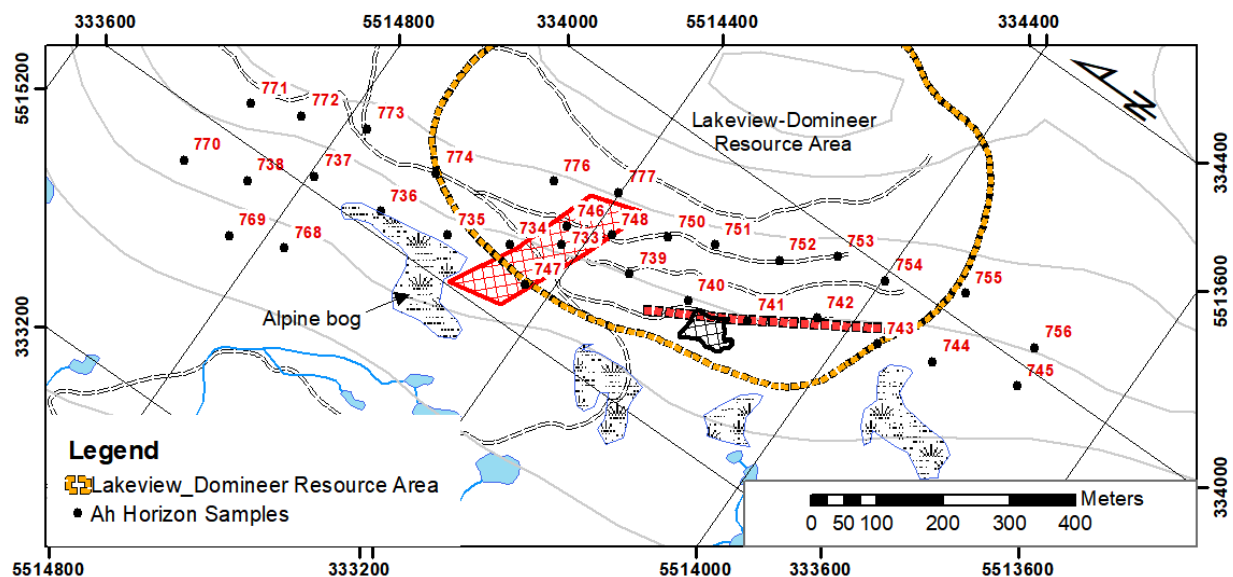
2 - Values in ppb

Abbreviations: Ah - Ah horizon soil (ME-HAL01); CC - Charcoal collectors (ME-HAL01a); Ah-Bio - Ah horizon Bioleach; MHF-Bio - Mountain hemlock foliage Bioleach; MHF - Mountain hemlock foliage (ME-HAL01a); RC - Resin collectors; TF - Transpired fluids; YCB - Yellow cedar bark (ME-HAL01a). Note that numeric counts do not include QC samples.

## Ah Horizon Soil

### LOI Results

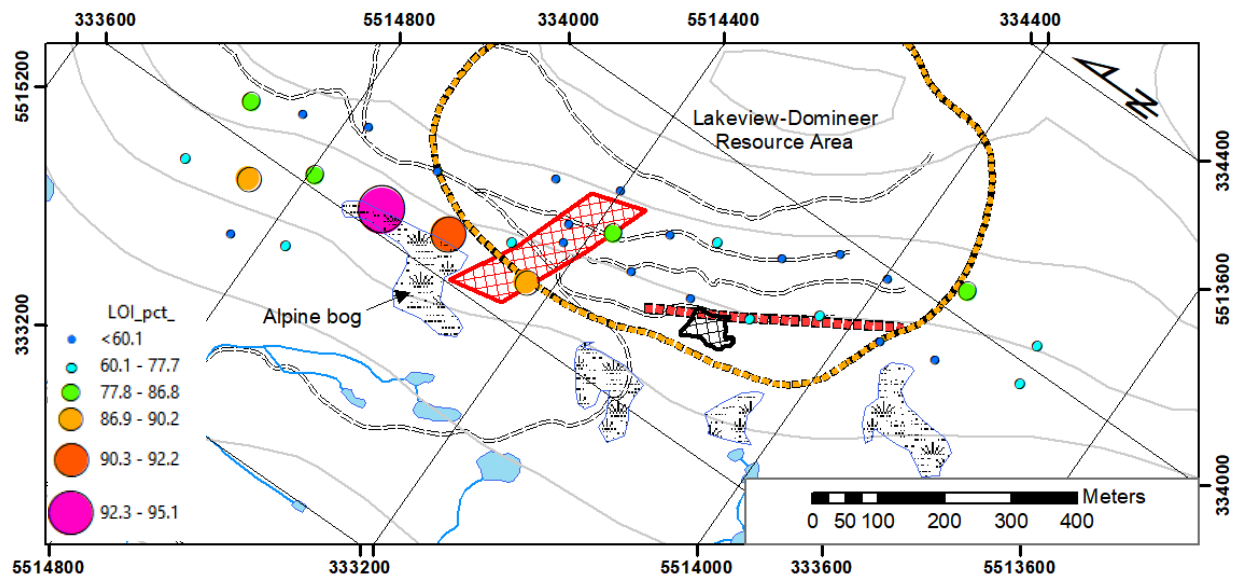
Figure 8 shows the Ah horizon sample locations. Note that samples could not be collected at every sample station: sites in bogs, and those with anthropogenic disturbance, or immediately downslope from old workings, or waste piles, were avoided.



**Figure 8:** Location of Ah horizon soil samples. Red hatching – observed mineralization, black hatching – dump of mineralized material at Domineer adit portal. Domineer vein shown as dotted red line.

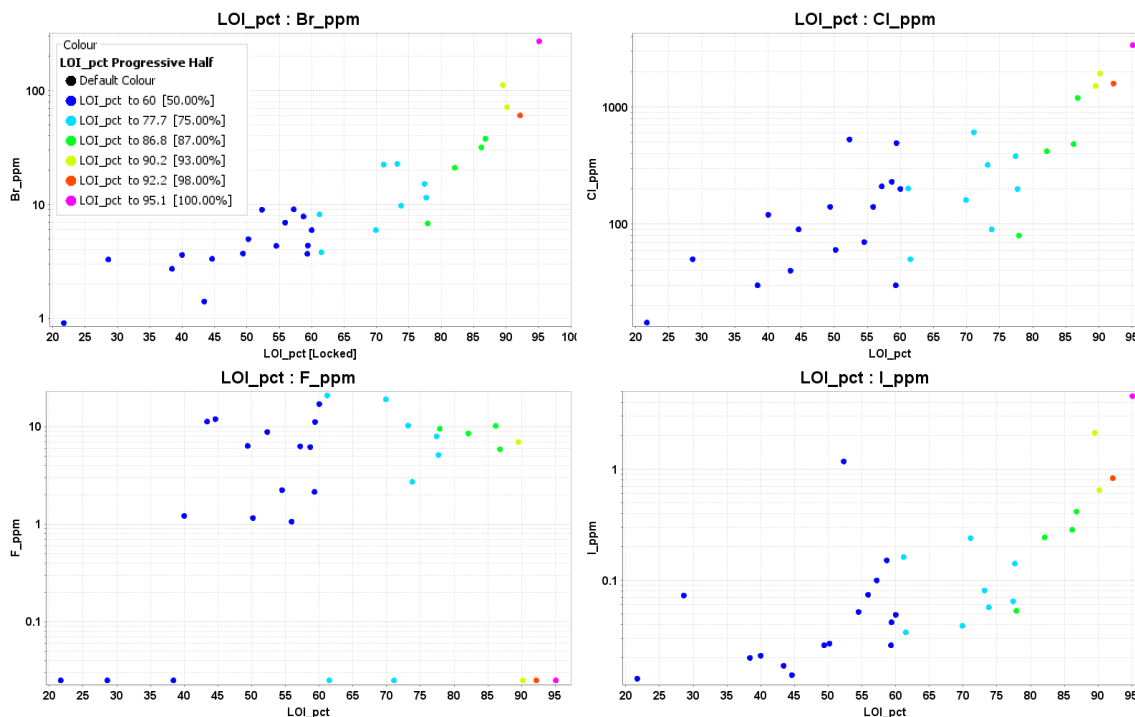
The Ah horizon is quite variable in texture across the area, varying from an organic-rich matrix in poorly drained areas to less organic-rich over well-drained colluvium. Variations in organic content are demonstrated by % LOI (loss on ignition) results shown in Figure 9. LOI averages 57.3% on the well-drained soils to the E and S of the mineralized zone, but is much higher to the N and W near the alpine bogs. The four highest values (Samples 735, 736, 738 and 747) all exceed 90% LOI (in the -80-mesh fraction)<sup>1</sup> and are from areas where either freshwater springs emerge at the surface or occur on saturated ground at the top end of alpine bogs.

<sup>1</sup> LOI determinations are done on the -177-micron fraction. Sample screening appears to enhance the organic component of the samples resulting in higher LOI results than would be expected from visual inspection of the whole sample.



**Figure 9:** Percent LOI in Ah horizon soils (-177 micron fraction).

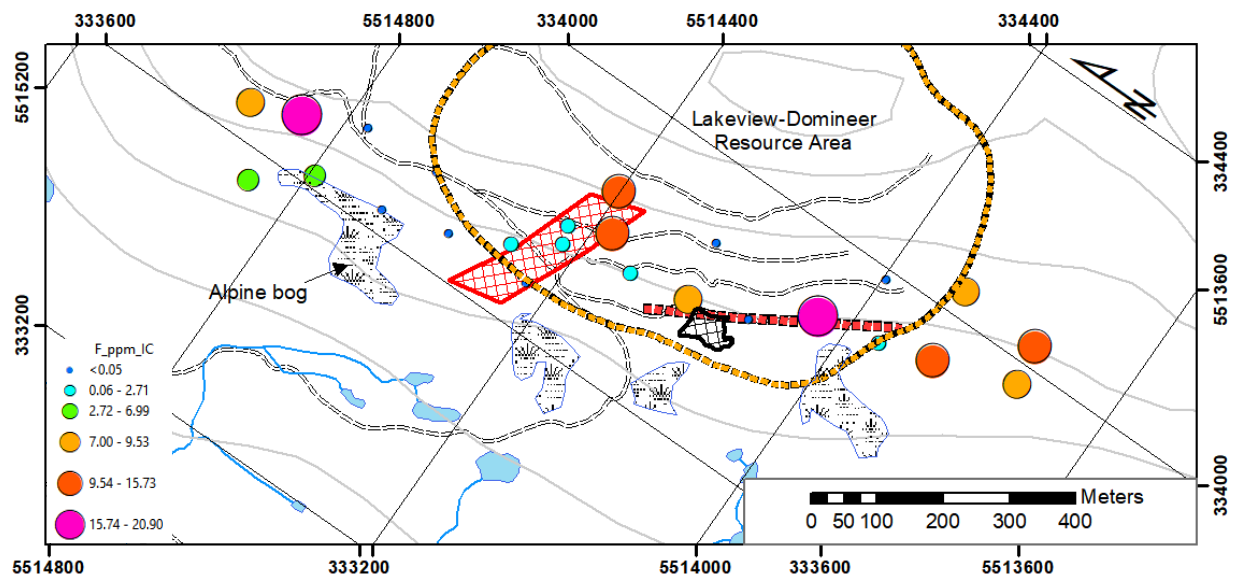
Figure 10 shows that halogens determined by the ME-HAL01 method show strong positive correlations with LOI in the Ah horizon suggesting that Br, Cl and I are likely to be present as organo-halogen compounds (Biester et al., 2017). This relationship appears to be preserved even after the samples have been ashed at 485 °C. Fluorine does not show a compelling correlation with LOI indicating that it is not bound to organic matter in the soil.



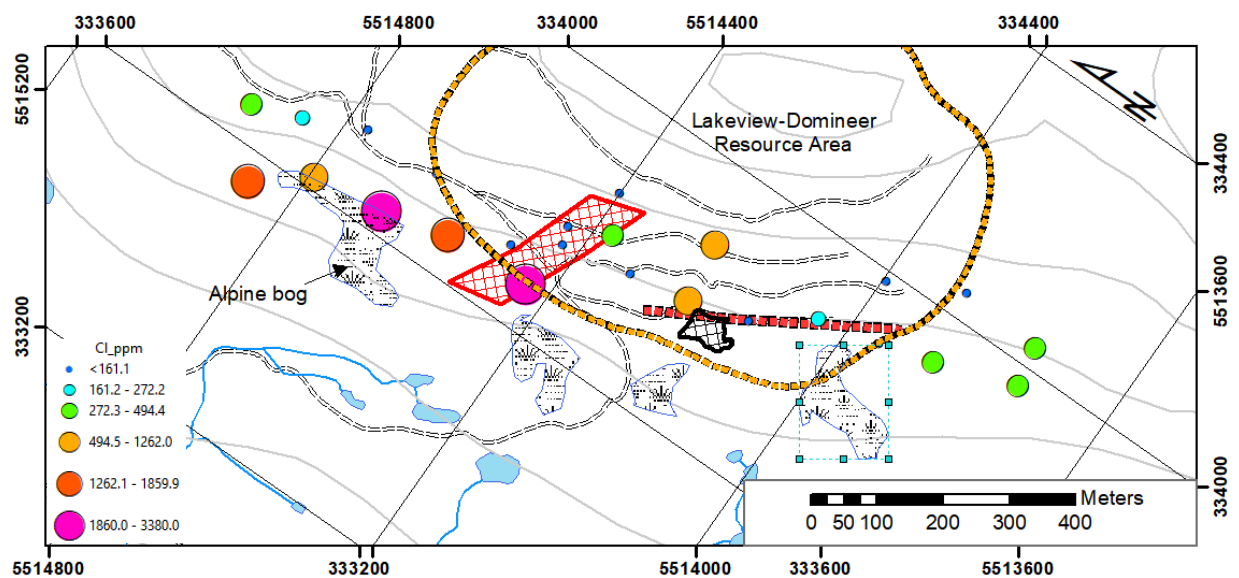
**Figure 10:** Correlations between Cl, Br and I and LOI. F does not show this relationship.

### ME-HAL01 Results

Ah horizon halogen results are plotted on Figures 11 to 14. Fluorine (Fig. 11), which is not correlated with LOI, shows an unremarkable pattern. Most of the samples over the central part of the transect display only background concentrations (<6.00 ppm), however two samples (10.5 and 12.0 ppm) overlying the southeastern limit of the breccia zone have anomalous concentrations. Furthermore, two anomalous values (8.8 and 20.9 ppm) also overlie the Domineer vein trend, however they are separated by a sample with a background concentration. Elevated F values are present near to the ends of the sample lines. In the NW, samples 771 and 772 show weakly to strongly anomalous concentrations of 8.53 and 17.1 ppm respectively. Both occur in areas with organic-rich Ah horizons indicated by LOI values of 82.1 and 60.0%: both samples occur close to freshwater seeps at the upper end of an alpine bog. At the SE end of the line, samples 744, 745 and 756 all have moderately elevated F concentrations (10.2, 11.2 and 7.9 ppm) and possibly indicate the southeastern continuation of the Domineer vein outside of the defined resource area.



**Figure 11.** Fluorine in Ah horizon soils – ME-HAL01.



**Figure 12:** Chlorine in Ah horizon soils – ME-HAL01.

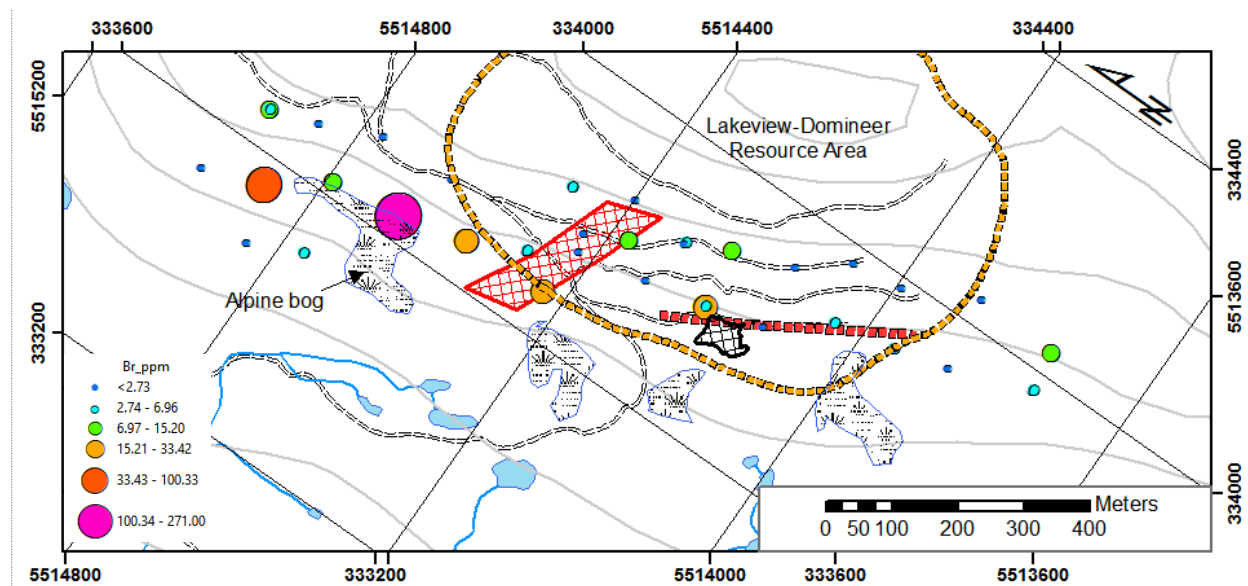
Interpretation of Cl, and I in the Ah horizon needs to consider the correlation of these elements with LOI (Fig. 10).

To the SE of the breccia zone, Cl concentrations (Fig. 12) are mostly at background levels (<494 ppm) although two weakly anomalous samples (740 and 751) highlight the area immediately up slope from the mine dump. Both samples are within the resource area and thus could represent expressions of the Domineer veins system.

More strongly anomalous concentrations extend from the breccia zone to the NW end of the sampled area and appear to closely follow the distribution of poorly drained organic-rich soils as previously discussed. One exception to this is sample 747 (1940 ppm) that lies over the breccia

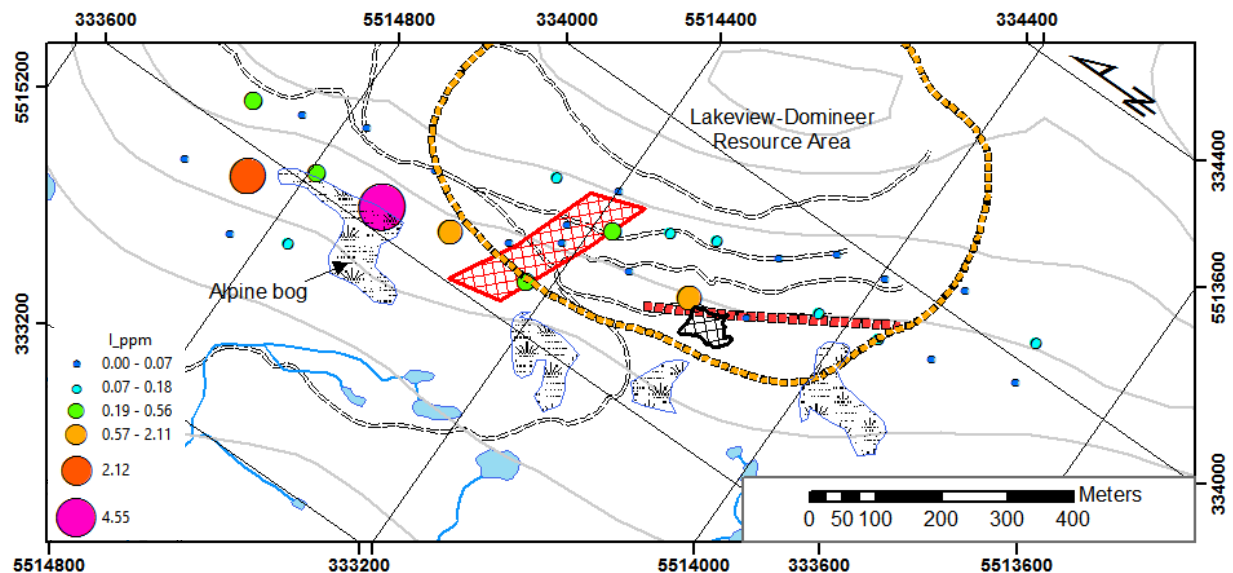
zone at a location that appears to be visually poor in organic matter, however the LOI of the soil at that locality (90.2%) indicates that it is indeed organic-rich thus explaining the elevated concentration.

Bromine and I results (Figs. 13 and 14) show similar patterns to Cl and LOI confirming that organic content of the soil is the primary concentration control. For Br (Fig. 13), elevated values extend from the breccia zone to the NW limit of sampling. The maximum concentration (271 ppm) occurs in sample 736, which is located above an alpine bog in an area of saturated ground. Strongly elevated concentrations also occur at samples 735 and 738 (60 and 112 ppm) and coincide with organic-rich samples associated with fresh water springs at the upslope limit of an alpine bog. Sample 747 is the only one with an elevated concentration directly overlying the mineralized zone.



**Figure 13:** Bromine in Ah horizon soils – ME-HAL01.

Iodine results (Fig. 14) show similar patterns to Br and display highest concentrations (2.12 and 4.55 ppm) in the poorly drained and organic rich soils at the NNW end of the transect. In the central part of the transect close to the breccia zone, values are somewhat elevated at stations 735 and 747, but there is no pattern suggesting that the responses are related to the mineralization. A single weakly anomalous sample (#740) is likewise noted on the Domineer vein trend close to the mine dump. It appears that this anomaly may be fortuitous as none of the other samples along the trend exhibit more than background concentrations.



**Figure 14:** Iodine in Ah horizon soils – ME-HAL01.

In summary, the Ah horizon ME-HAL01 results do not effectively define the mineralized zones. Rather, halogen concentrations appear to be controlled the soil's organic content and degree of water saturation. Therefore, this medium is unlikely to be effective for identifying halogen anomalies around mineralized occurrences.

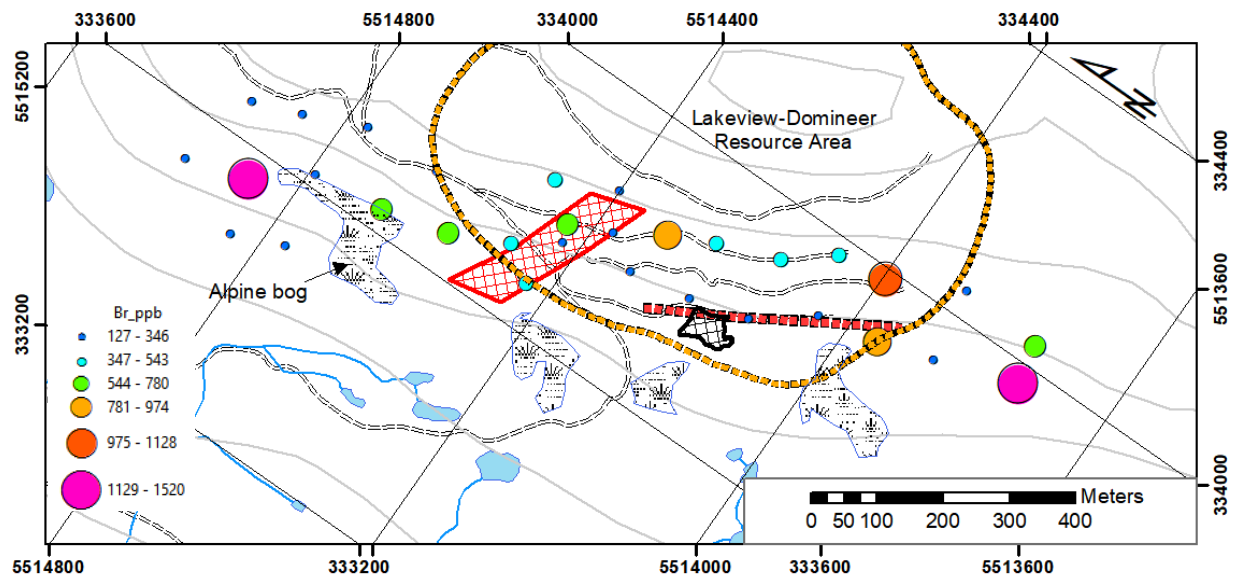
## Ah Horizon Bioleach Results

Bioleach, the second method applied to the Ah horizon soil, has the capability to determine Br and I to very low concentrations. Results for these elements are presented in Figures 15 and 16.

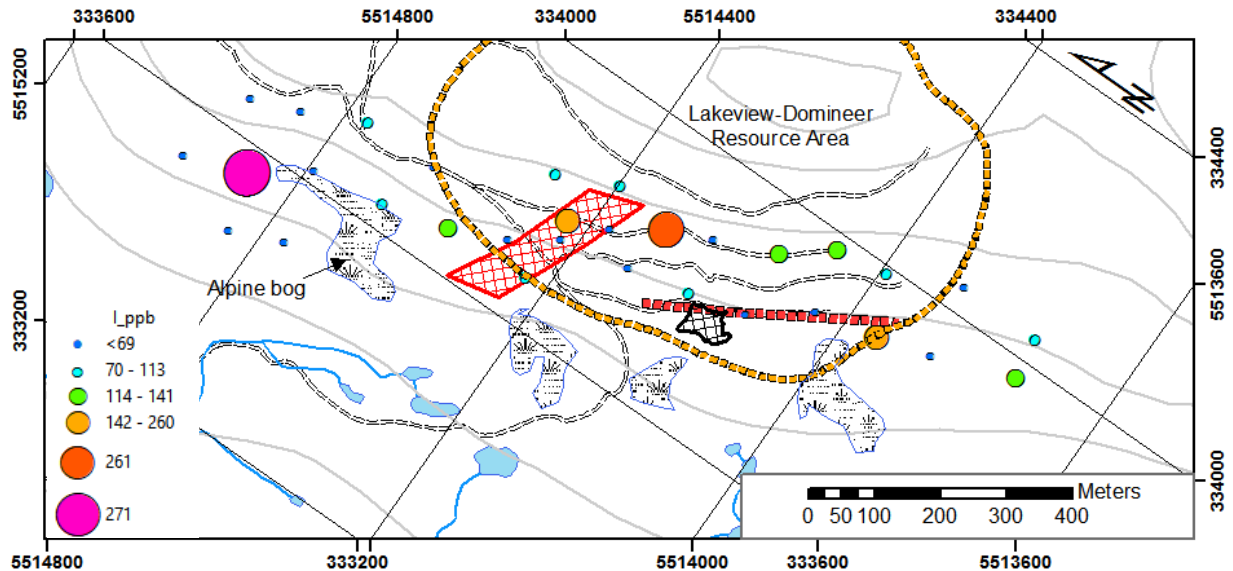
Bioleach Br (Fig. 15) displays consistently low concentrations over the central parts of the sample transects. There is no discernable response over the mineralized zones but elevated values are present at the SSE end of the line along the projected strike of the Domineer vein. Elevated concentrations occur in a relatively well-drained area characterized by a thin veneer of colluvium and scattered outcrops of Nanaimo Group sediments. The responses are interpreted to reflect the presence of the subcropping Domineer vein system. A single anomalous sample at the NNW end of the line (sample 738) corresponds to a site with high organic content at the edge of a small creek gully. The high Br concentration (1520 ppb) is interpreted to be a hydromorphic response associated with the drainage channel.

Iodine (Fig. 16) appears to discriminate the breccia zone slightly better than Br. Two moderately anomalous samples (746 and 750); one over the trend of the zone and one slightly to the SSE mark the position of the mineralized breccia body. A weak response is also present over the SSE extent of the Domineer vein. The maximum concentration (271 ppb), as seen for Br, occurs in sample 738 at the NNW end of the line. The high I concentration is also interpreted to be a hydromorphic effect.

As observed in the ME-HAL01 results, the halogens in Bioleach on Ah horizon soils do not appear to effectively discriminate the known mineralized zones. Weak responses over the Domineer vein are overwhelmed by strong probable hydromorphic responses at the NNW end of the line.



**Figure 15.** Bromine Ah horizon soils - Bioleach.



**Figure 16.** Iodine in Ah horizon soil – Bioleach.

## ***Halogens in Ion Collectors***

Textural and compositional variations of the Ah horizon soils clearly exert a strong influence on the concentrations of the halogens. Concentration differences caused by variations in organic matter content appear to overwhelm any definitive signals coming from the mineralization. The use of ion collectors provides a potential mechanism to eliminate these matrix effects. The collectors are designed to capture halogens emanating from the ground and to trap them on a medium with a highly consistent matrix, and in so doing eliminate much of the extraneous variability.

### **Charcoal Collector Results**

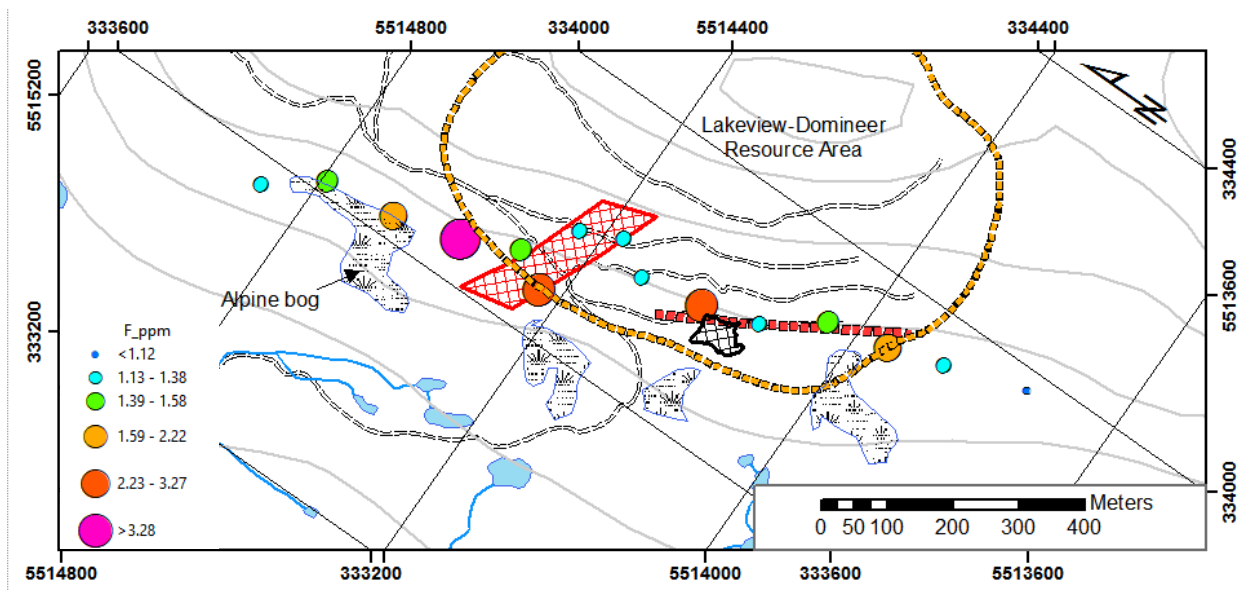
#### **ME-HAL01a**

ME-HAL01a results for the charcoal ion collectors are presented in Figures 17 to 20. Fluorine (Fig. 17) displays a two-sample anomaly over the breccia zone with concentrations decreasing gradually to the NNW. South of the breccia zone in the well-drained colluvial cover, values are generally more subdued and approach background levels. There is no convincing response on the Domineer vein trend although there is one sample with a moderately elevated value near the northern limit of the vein.

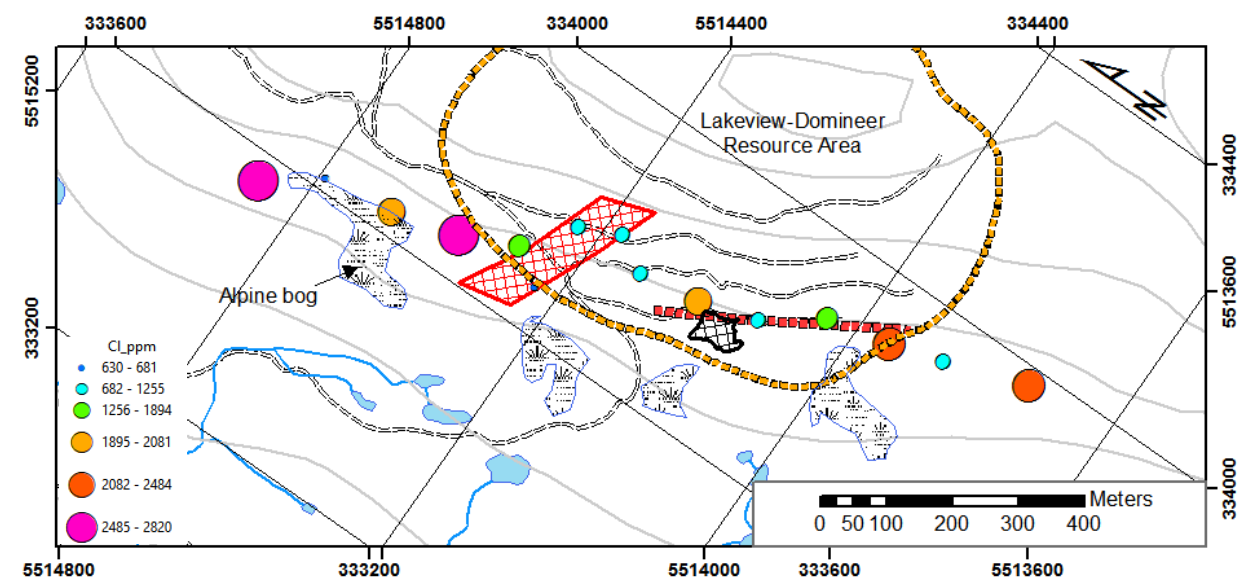
Chlorine (Fig. 18) displays noisy results with no coherent patterns related to the position of either of the mineralized zones. Samples with the strongest responses coincide with locations close to springs (samples 735 and 738) suggesting that Cl flux is highest in the wetter areas; there is no convincing response in the better drained southern half of the line. Values over the Domineer vein are relatively low and only show slight enrichment at the southern end of the transect. Those responses are unconvincing and cannot be conclusively related to the presence of vein mineralization.

Bromine (Fig. 19) has two elevated values (28 and 18 ppm) that occur on either side of the breccia zone. These responses can perhaps be interpreted as a ‘rabbit-ear’ feature around the mineralized zone. Similar Br responses are observed at the Lara project (Heberlein et al., 2017a) and are well documented by Trofimov and Rychkov (2004) in a variety of mineralization settings.

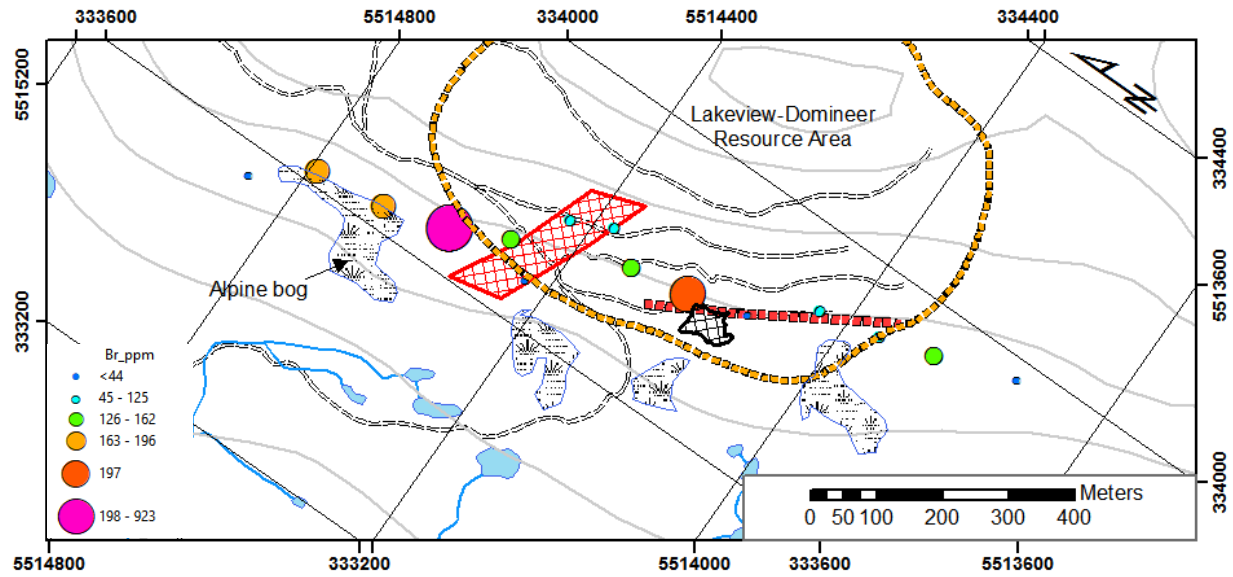
Iodine results are more compelling than the other halogens. Figure 20 shows that I displays a moderate to strong response over the breccia zone and that elevated concentrations extend to the SSE along the Domineer vein trend. High organic and spring sites that have proven to concentrate halogens in the Ah horizon soil appear to be unenriched in this element in the charcoal collectors. This reduces the possibility that the I response is related to endogenic processes in the soil and implies that the response in the charcoal collectors is exogenic in nature. The maximum concentration (0.26 ppm) occurs at the SSE end of the transect in a pair of anomalous responses overlying the projected continuation of the Domineer vein trend.



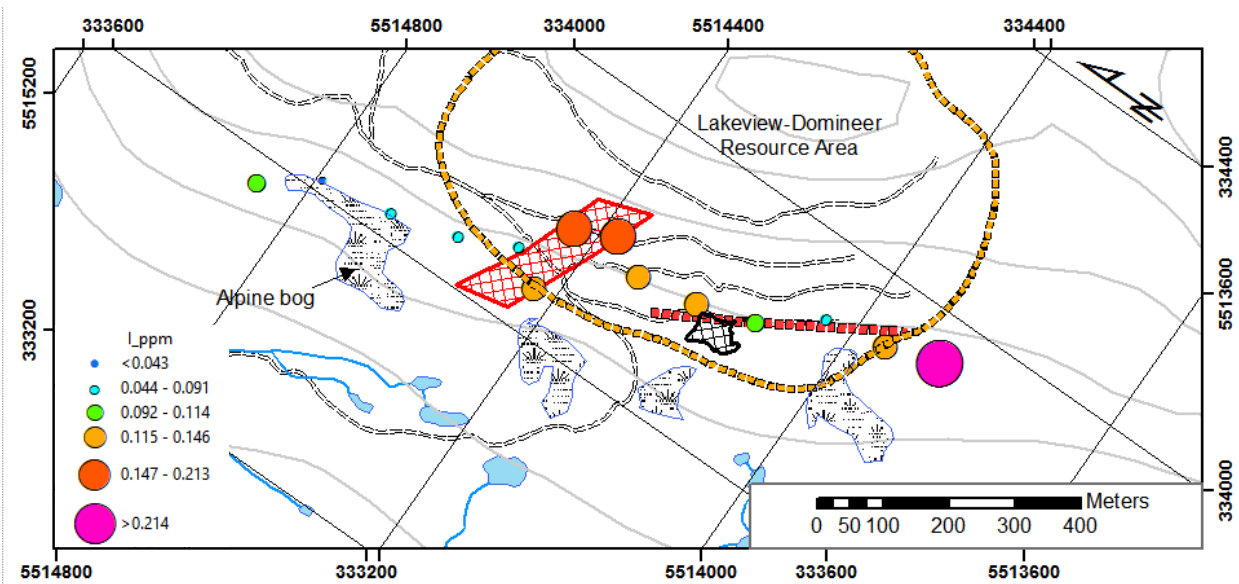
**Figure 17:** Fluorine in charcoal ion collectors – ME-HAL01a.



**Figure 18:** Chlorine in charcoal ion collectors – ME-HAL01a.



**Figure 19:** Bromine in charcoal ion collectors – ME-HAL01a.



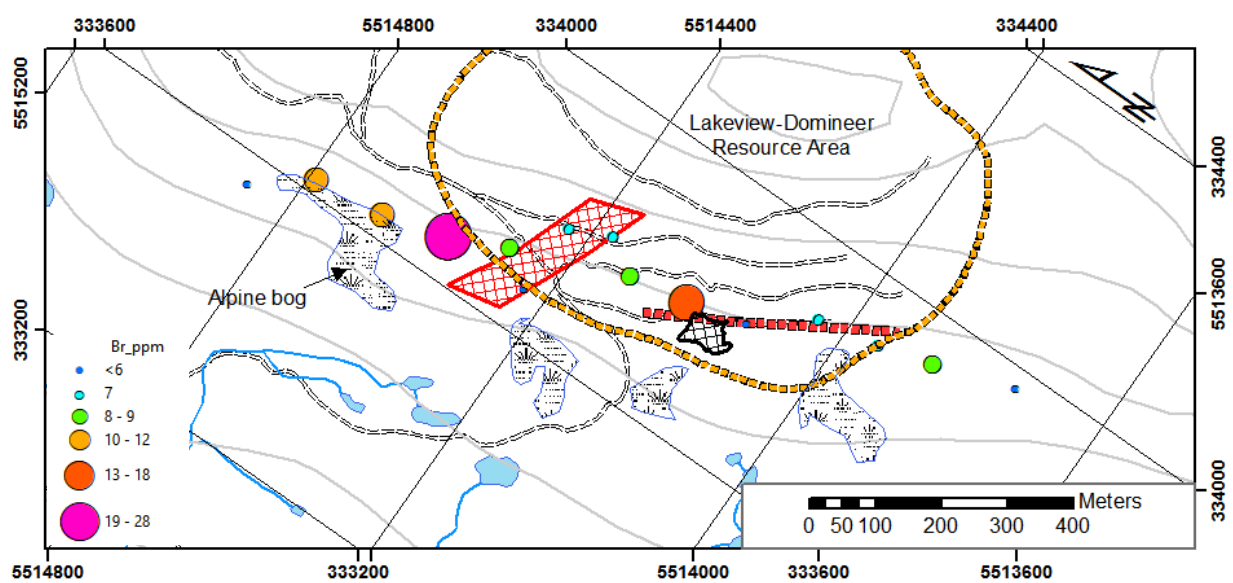
**Figure 20:** Iodine in charcoal ion collectors – ME-HAL01a.

### Sodium Pyrophosphate (ME-MS07)

Charcoal collectors were analyzed for Br and I by a second method - a sodium pyrophosphate leach. Sodium pyrophosphate is a commonly used leach for the extraction of metal ions bound to fulvic and humic acids in soil and humus samples (Hall et al., 1996). It is therefore an ideal technique to investigate weakly bound ions adsorbed onto the charcoal collectors.

Bromine results are shown in Figure 21. They closely match the patterns produced by the HAL-01 leach (Fig. 19) and show what appears to be a possible rabbit-ear response bracketing the breccia zone. Furthermore, unlike the ME-HAL01 results, the sodium pyrophosphate leach defines a Br low directly over the breccia zone. Depletion over the mineralization with rabbit ear peaks on either side is a distinctive feature of the Br haloes described by Trofimov and Rychkov (2004).

Chlorine is not detected by this method and the I results were all below lower detection limit of 0.05 ppm.



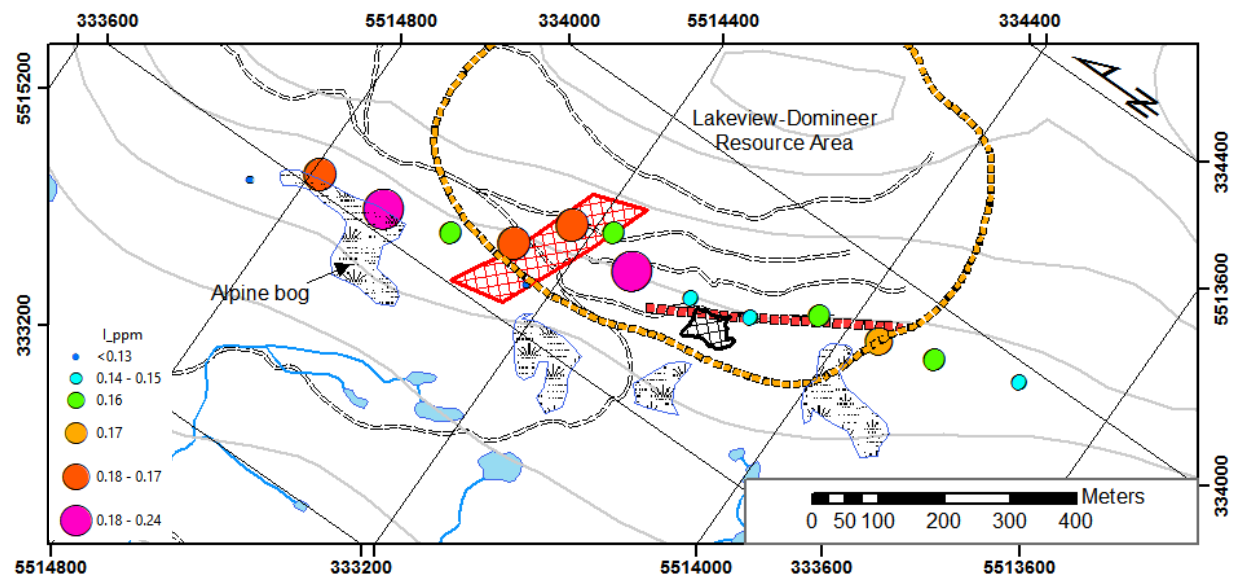
**Figure 21:** Bromine in charcoal collectors - sodium pyrophosphate leach.

### Deionized water leach (ME-MS03)

To further assess the I concentrations of the charcoal collectors, a 1g aliquot of charcoal was leached with deionized water and I was determined by ICP-MS. Results are shown in Figure 22. The water leach produces comparable results to ME-HAL01 but with lower contrast. Elevated values occur over the breccia zone mineralization but samples with similar concentrations are also present adjacent to the alpine bog near the NNW end of the line. This result shows that the charcoal collectors accumulated I from the organic-rich, poorly drained environment near to the alpine bogs and therefore this signal could be an expression of I release from an already enriched substrate. Soil I enrichment, as demonstrated by the Ah horizon results, is likely caused by the formation of organo-halogen compounds in and around the bogs. Results show that I is probably being released from the ground in those areas. In contrast, the I response detected over the

breccia zone, where soils are thin and organic poor, most likely indicate direct release of I from the bedrock.

Elevated I values are not present along the trend of the Domineer vein, where concentrations are mostly at background levels. While defining anomalies in geologically meaningful places, this leach is less discriminating than the ME-HAL01 methods and appears to be more affected by endogenic processes at the sample sites.



**Figure 22:** Iodine in charcoal collectors – H<sub>2</sub>O leach.

## Resin Collectors

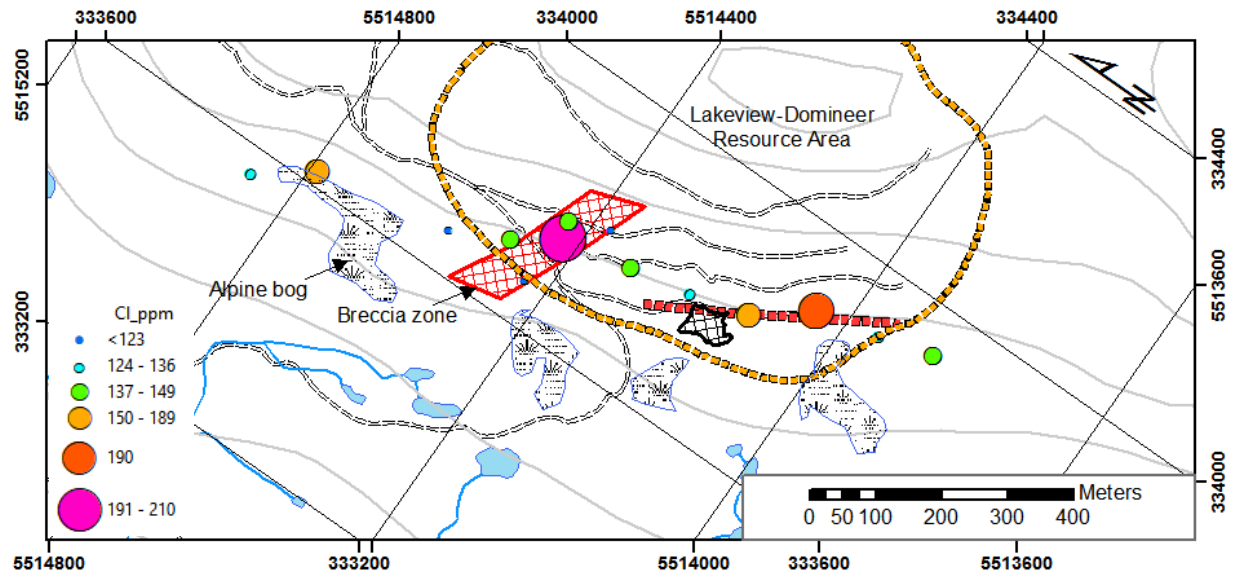
### Deionized Water Leach

Analysis of the resin collectors could not be done with the ME-HAL01 method, because the resin completely volatilizes during the ashing process. Instead a deionized water leach was used to determine Cl, Br and I by ICP-MS. Results are presented in Figures 23 to 25.

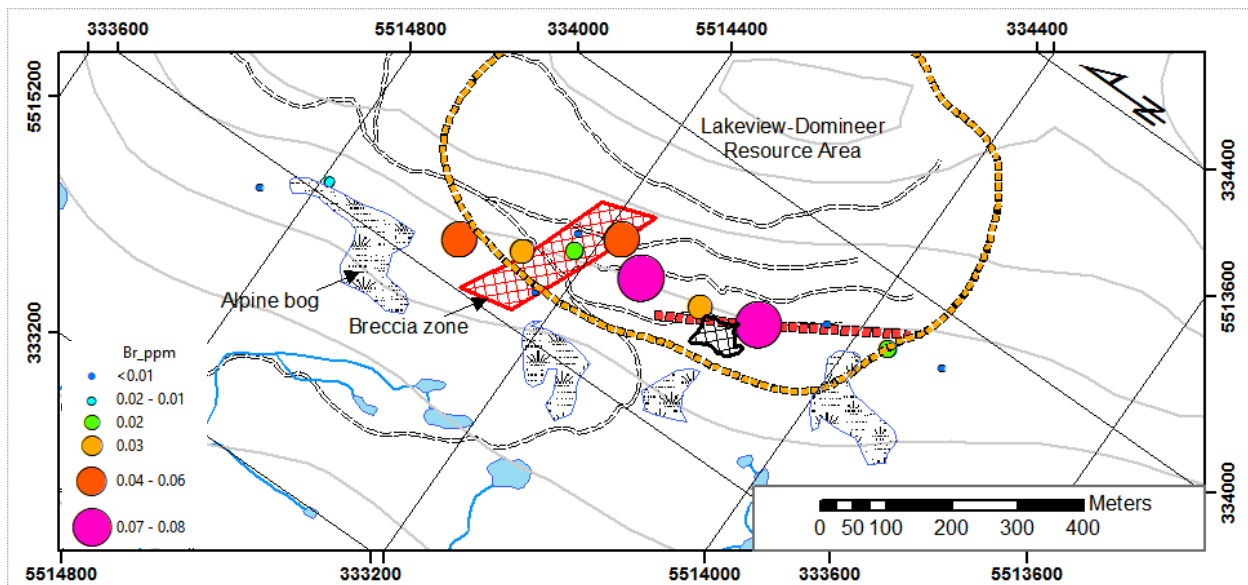
Chlorine results (Fig. 23) show a relatively flat background over most of the transect. Four samples with elevated values are present: one over the breccia zone (733), two on the trace of the Domineer vein (741 and 742) and one near the NNW end of the transect (737). Three of these are spatially related to the known mineralization but sample 737 coincides with an alpine bog site.

A strong response to the mineralization is displayed by the Br results. Figure 24 shows a now familiar pattern for this element with a low or depletion directly over the breccia zone and a strong response on either side. Two anomalous samples are also present on the trace of the Domineer vein.

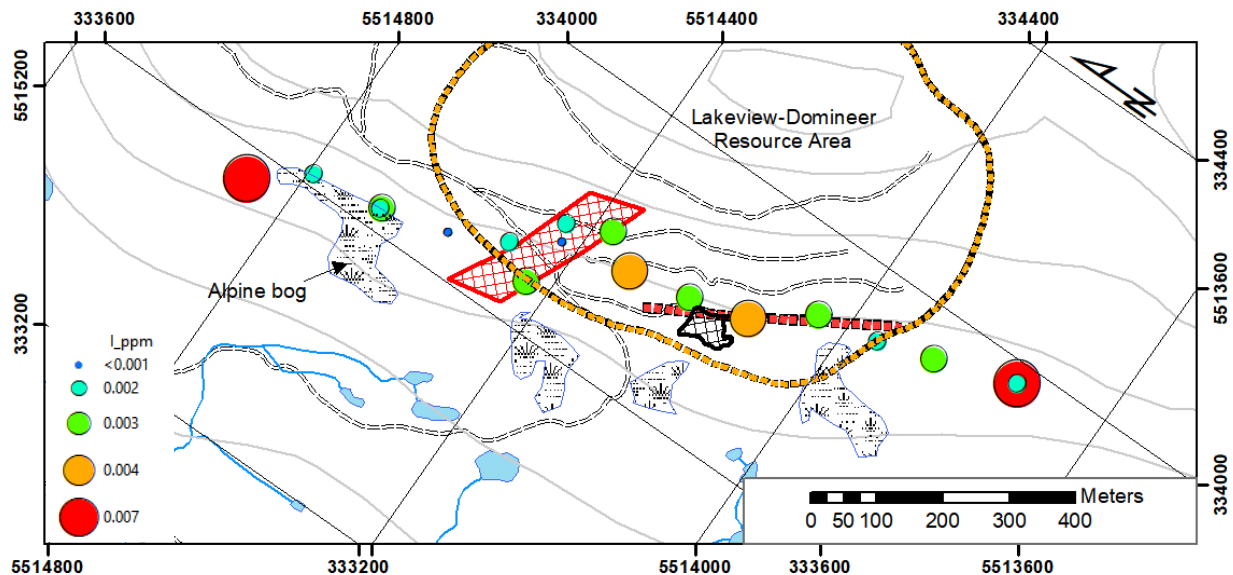
Iodine results (Fig. 25) show very little contrast and no clear patterns. The Domineer vein trend appears to have broadly elevated values but concentrations are so low that it is impossible to say with certainty whether the patterns are geological in nature or just reflect poor precision close to the detection limit. The latter is suspected. There is no convincing response at the breccia zone and to the NNW values show little variation above background levels except for the most northerly sample, which has the maximum I concentration (sample 738 – 0.007 ppm).



**Figure 23:** Chlorine results for the deionized H<sub>2</sub>O leach of resin ion collectors.



**Figure 24:** Bromine results for the deionized H<sub>2</sub>O leach of resin ion collectors.



**Figure 25:** Iodine results for the deionized H<sub>2</sub>O leach of resin ion collectors.

### **Cold Hydroxylamine Hydrochloride leach (ME-MS05)**

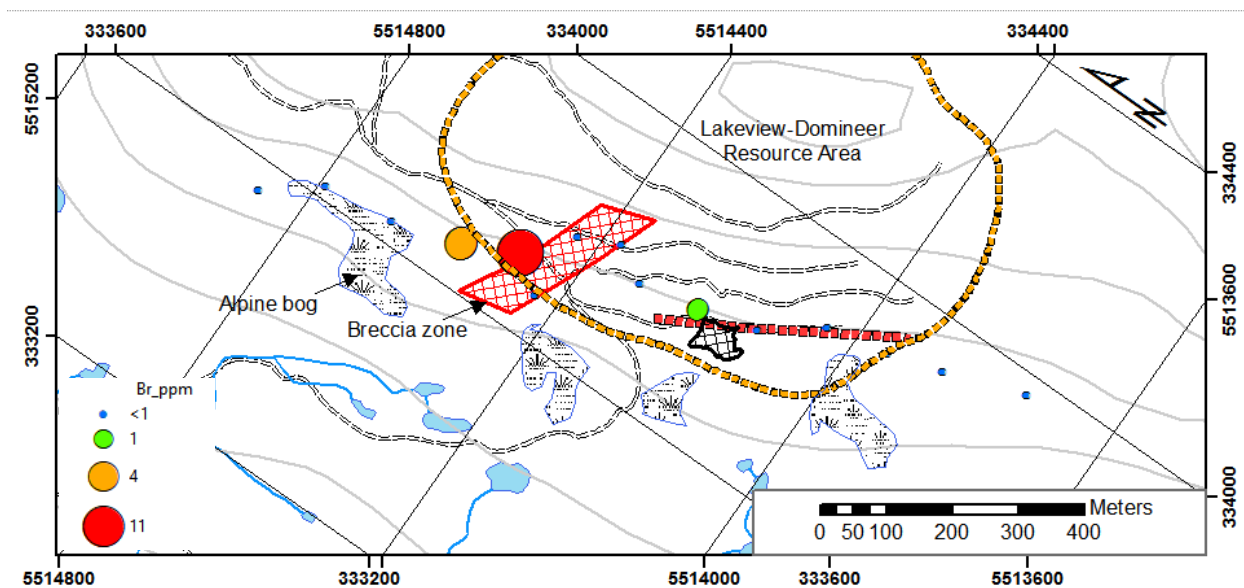
A cold hydroxylamine hydrochloride leach was used as alternative method to desorb weakly bound halogen ions from the resin collectors. Only Br and I could be analyzed by ICP-MS, because the leach solution contains Cl.

Bromine results are presented in Figure 26. Values show little contrast over much of the line with most falling below detection limit. Three higher values are present however. Two of them (734 – 11ppm and 735 – 4 ppm) lie on the WNW flank of the breccia zone. The third elevated sample (740) with a much lower value of 1 ppm, occurs over the NNW limit of the Domineer vein trend. This pattern could reflect the same kind of rabbit-ear response discussed above for the charcoal collector results. Whether it does or not, the results show that detectable Br only occurs near the known mineralization.

Iodine results for this leach are all below the lower detection limit.

### ***Halogens and Anions in Vegetation***

Investigation of halogen concentrations in the most common tree species took advantage of a previous biogeochemical study that was carried out by the GSC in 1990 (Dunn, 1995). Archived samples from the GSC study were available for reanalysis using the methods developed as part of this investigation. New sampling was limited to mountain hemlock foliage. This was augmented with archived Yellow-cedar bark (YCB) ash samples from the GSC archive. Sample locations for each medium are shown in Figure 27. Note that the 1990 and 2016 sample locations are slightly different reflecting the distribution of each species along the transect.

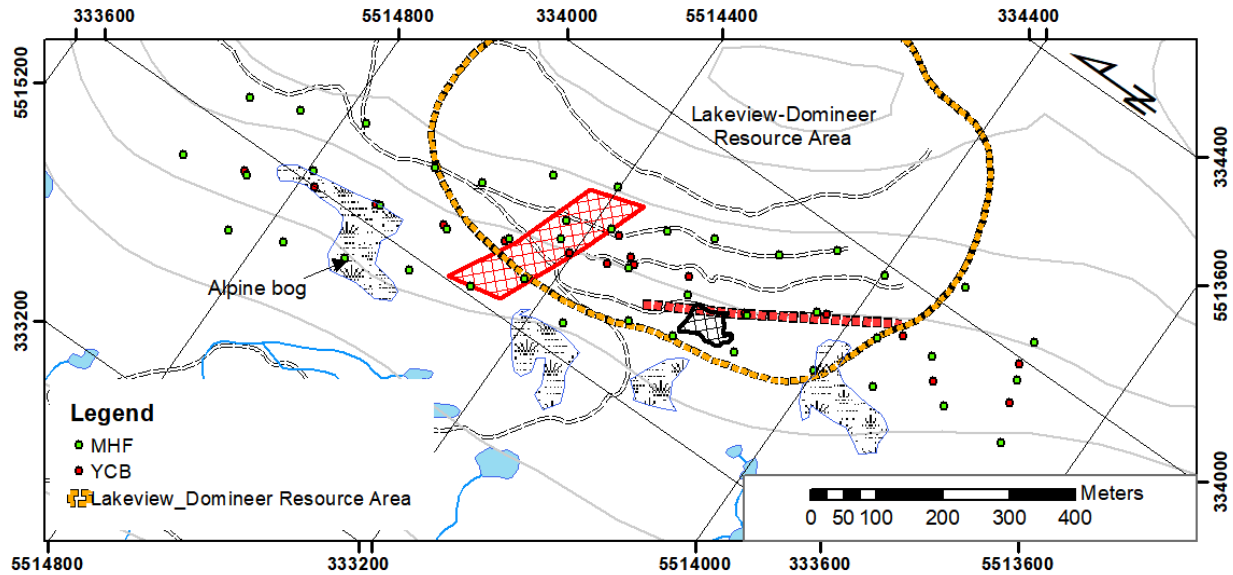


**Figure 26:** Resin ion collectors - Bromine in cold hydroxylamine hydrochloride leach.

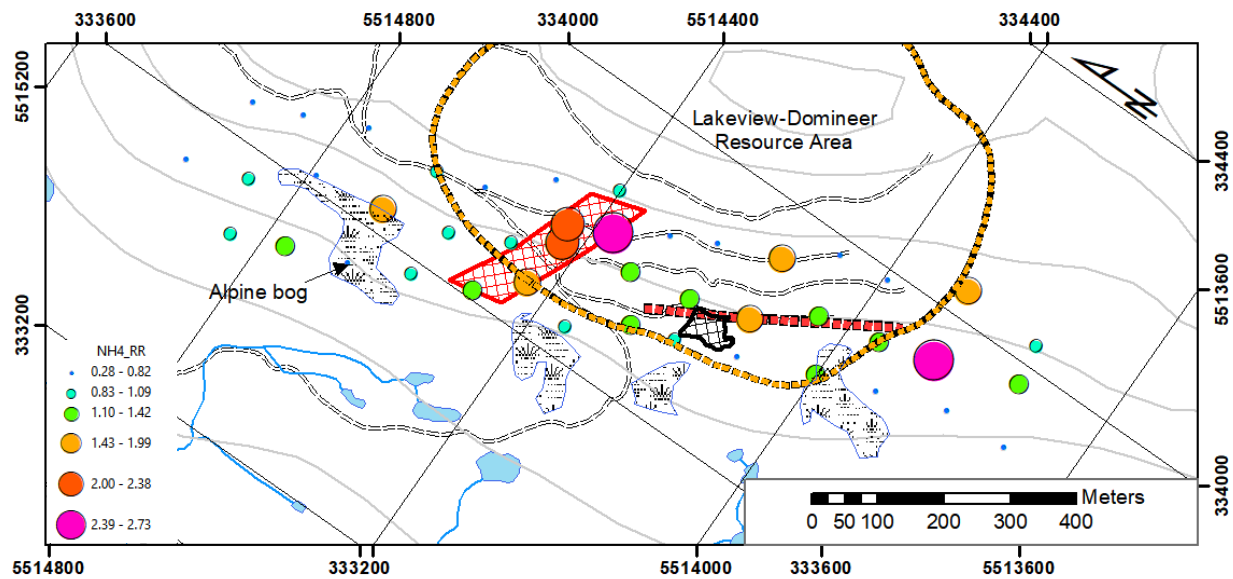
## Mountain Hemlock Foliage (MHF)

### Auto Analyzer: ammonium, phosphate and sulphate results

Of the anions determined by HPLC-IC, ammonium ( $\text{NH}_4$ ) reveals the most robust pattern over the known mineralization. Figure 28 shows a response ratio plot of the  $\text{NH}_4$  concentrations for MHF. Results show a very flat background away from the mineralization. Ammonium does not appear to be influenced by the presence of wetlands or organic-rich soils as has been observed for the halogens in other sample media. Anomalous results only occur close to mineralization with a cluster of three anomalous to highly anomalous samples directly overlying the breccia zone; and two, albeit widely spaced, anomalous samples along the Domineer vein trend. In terms of absolute concentrations, the breccia zone samples range between 94.7 ppm and 116.9 ppm compared to a typical background value of about 41 ppm.



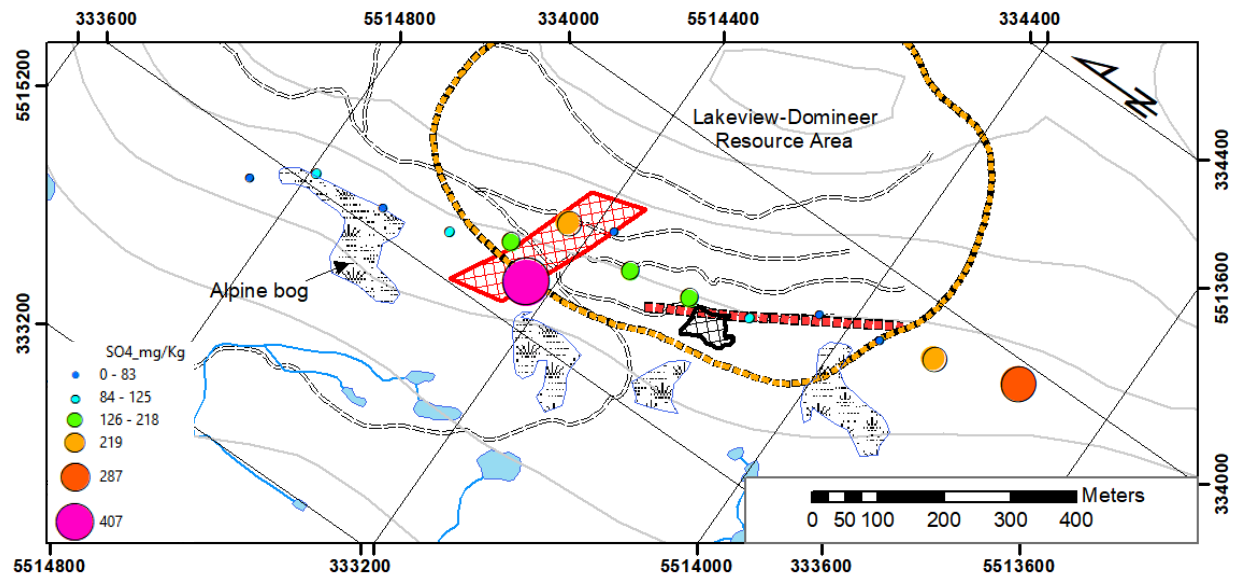
**Figure 27:** Sample location for MHF and YCB samples.



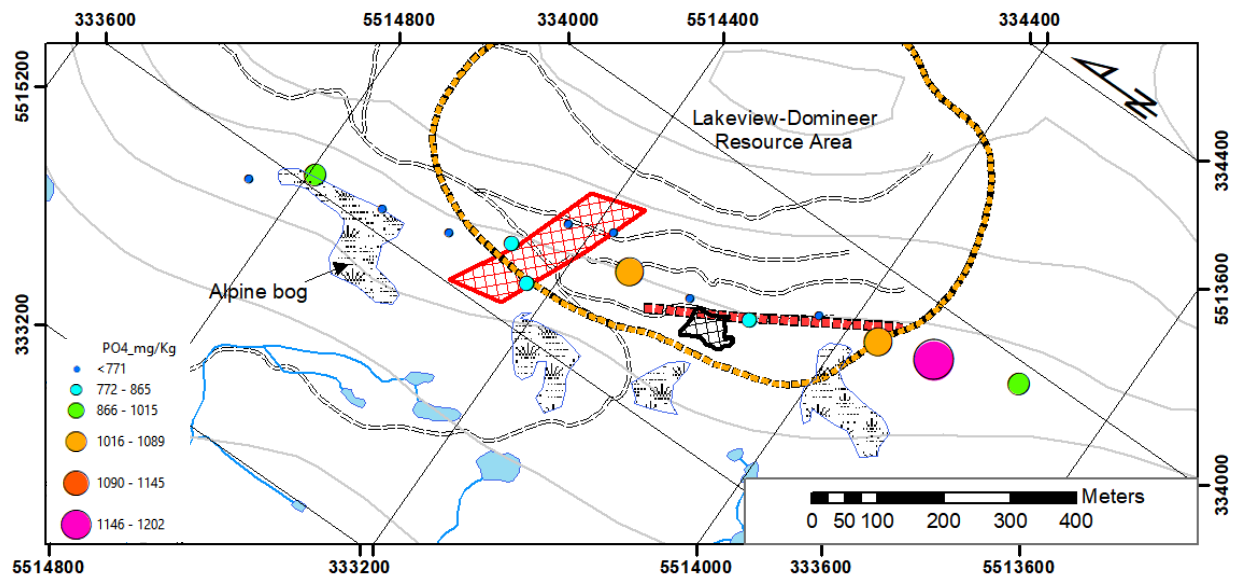
**Figure 28:** Mountain hemlock foliage - ammonium (response ratio) in H<sub>2</sub>O leach results.

Sulphate (Fig. 29) in MHF shows a similar pattern to NH<sub>4</sub>. Background is quite flat in the northern part of the line indicating that hemlocks in the poorly-drained, organic-rich areas are not enriched in SO<sub>4</sub>. More variation in SO<sub>4</sub> concentrations occur on the well-drained, southern half of the transect, showing that the trees in that area are taking up more of this anion, which is almost certainly derived from the sulphide-rich Domineer vein. Well defined anomalies are observed in two places: a high-contrast, two sample response (219 and 406 ppm) located directly on top of the breccia zone and a second strong response in the southern two samples along the Domineer vein trend (286 ppm).

Phosphate results are less compelling. Figure 30 shows that most of the samples contain only background concentrations. There is no anomalous response over the breccia zone or most of the Domineer vein trend; however, values are elevated at the SSE end of the line. A lack of a  $\text{PO}_4$  response is unsurprising as P is known to be an essential element for plant growth and many species can regulate their P uptake from the soil (Schachtman et al., 1998). Furthermore, there is no reason to expect that the mineralized areas would be enriched in P.



**Figure 29:** Mountain hemlock foliage - sulphate in  $\text{H}_2\text{O}$  leach results.

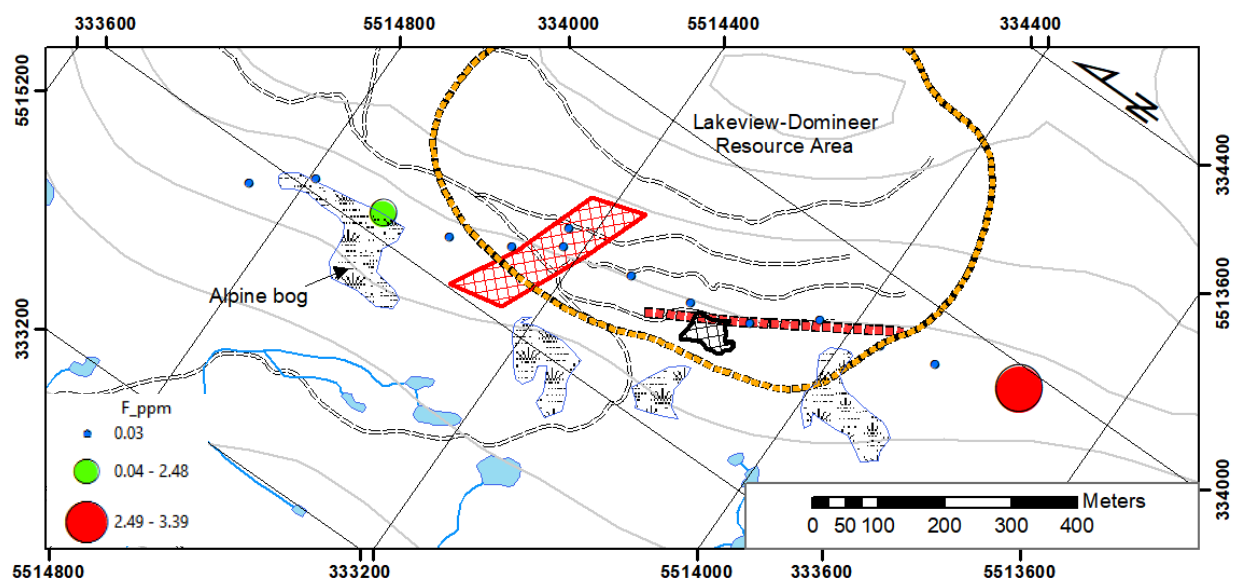


**Figure 30:** Mountain hemlock foliage - phosphate in  $\text{H}_2\text{O}$  leach results.

## Halogens in mountain hemlock foliage – ashed tissues

The following figures illustrate the halogen results from the ME-HAL01 method for the ashed mountain hemlock foliage samples. Fluorine is determined by IC and Cl, Br and I by ICP-MS.

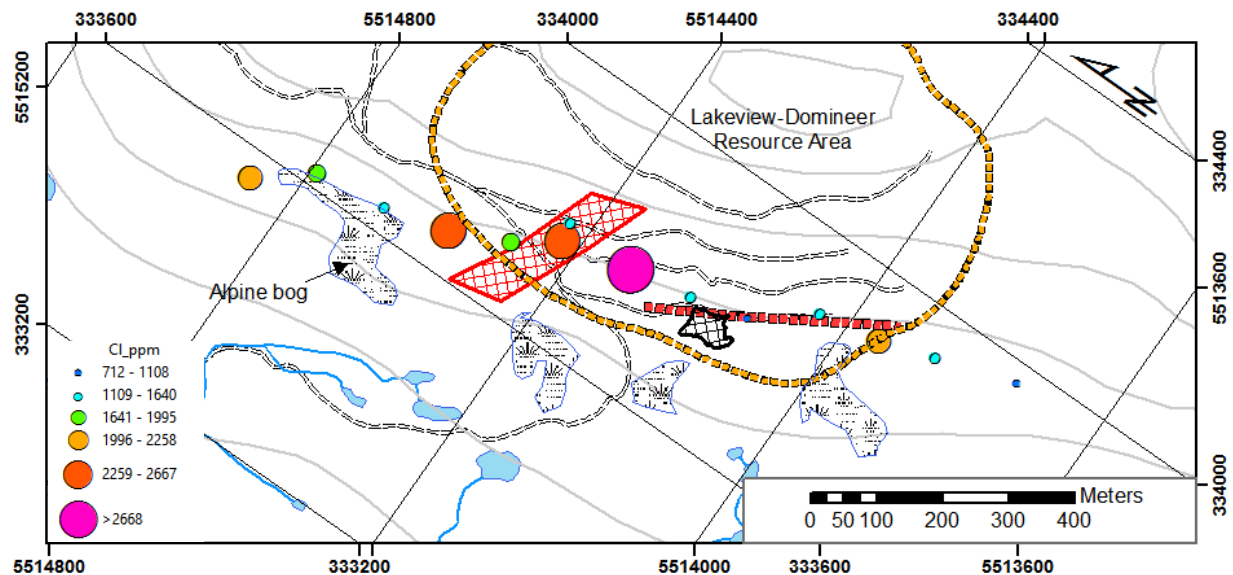
Fluorine values (Fig. 31) are mostly at the 0.05 ppm method detection limit, however two samples (736 and 745) display detectable concentrations. Sample 736 lies just up-slope from an alpine bog in an area of saturated ground and 745 is on a well-drained colluvium covered slope. Little significance can be attributed to these results.



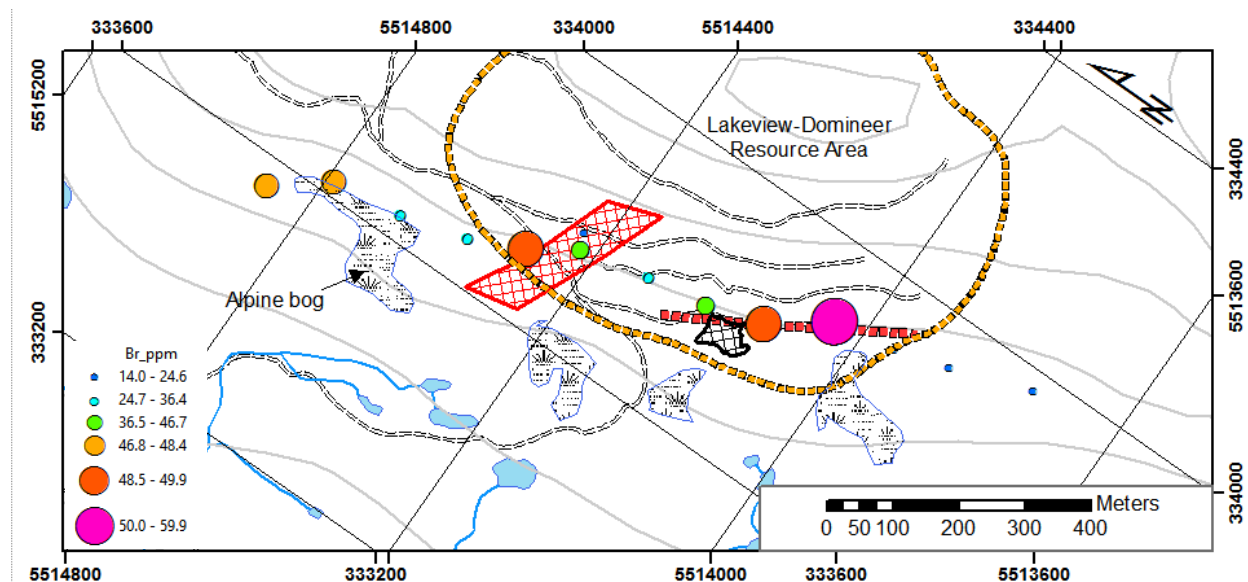
**Figure 31:** Mountain hemlock foliage – F by IC.

Chlorine (Fig. 32) shows a much more convincing pattern. Values at the northern and southern extremities of the transect display only background variations. However, over the breccia zone there is a broad anomalous response. Highest Cl concentrations occur at distances approximately 100 m on either side of the mineralized zone suggesting rabbit-ear response. Between these peaks values are moderately elevated, forming a subtle apical anomaly. There are no anomalous values on the Domineer vein trend. This may indicate a fundamental difference in the halogen chemistry of the two styles of mineralization (i.e. the breccia zone may be more Cl rich).

Bromine patterns are quite different from Cl. Figure 33 shows that the breccia zone is defined by just a single moderately anomalous sample (734) located over the NNW edge of the zone. Elevated values highlight the Domineer vein trend with one moderately and one strongly anomalous sample located over the middle of the trend.

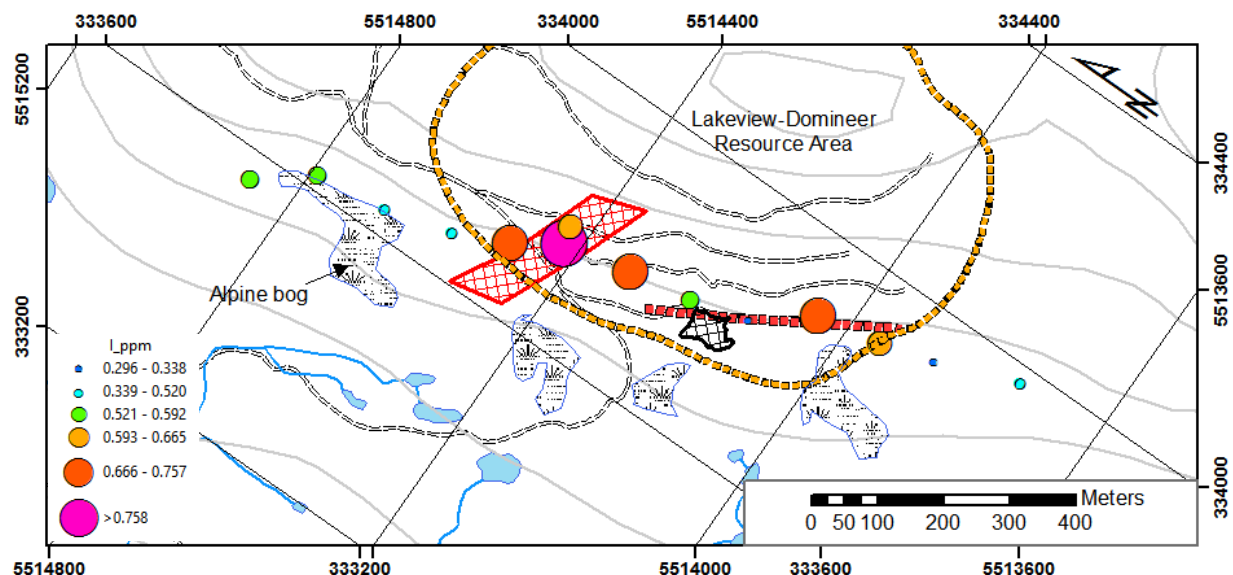


**Figure 32:** Chlorine in ashed Mountain hemlock foliage.



**Figure 33:** Bromine in ashed mountain hemlock foliage.

Both mineralized zones are clearly visible in the I results (Fig. 34). At the breccia zone, it defines a broad apical response extending beyond the limits of the observed mineralization. The maximum concentration (0.957 ppm) lies directly over the mineralized zone. This sample is flanked by slightly less anomalous values. Two moderately elevated I values also mark the position of the Domineer vein trend. Background values at the northern and southern ends of the line are quite flat. There is no evidence of I enrichment in hemlocks growing in the organic-rich soils close to the alpine bogs in the NNW. Results suggest that the mountain hemlocks are responding to bedrock halogens concentrations and not variations in the soil organic content.



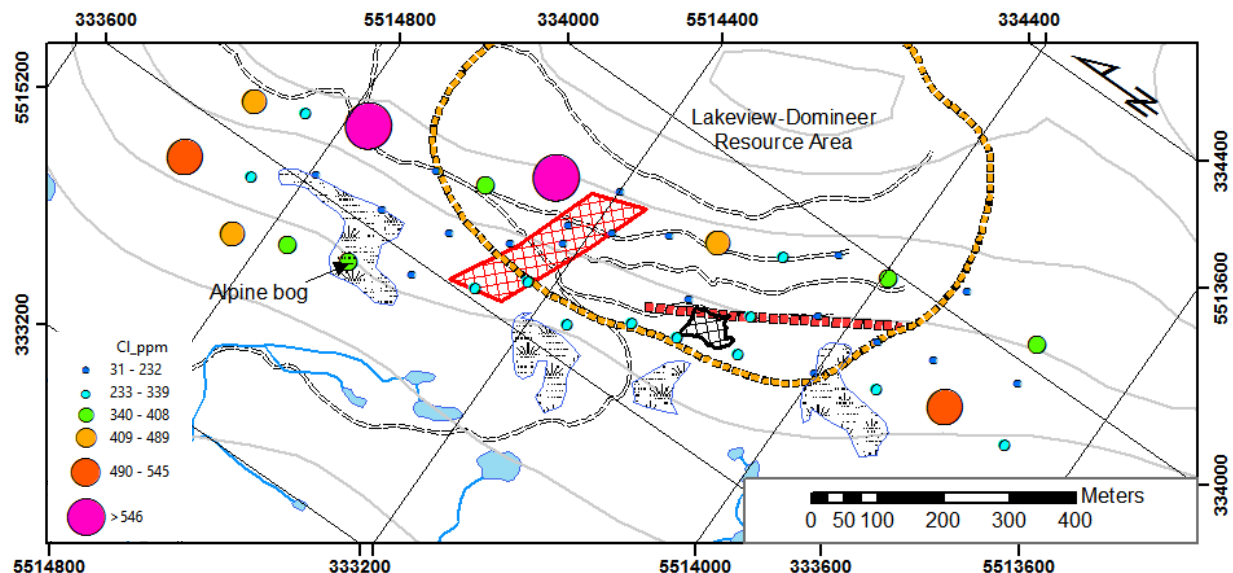
**Figure 34:** Iodine in ashed mountain hemlock foliage.

### Halogens in mountain hemlock foliage – Dry milled tissue

An analysis of the extended MHF sample set by ME-HAL01a was carried out on dry milled needles. Results provide a valuable comparison with the ashed tissue analyses described above and highlight the potential advantages and disadvantages of the ashing procedure. Chlorine analysis was done by IC and Br and I by ICP-MS on the water leachate. Fluorine could not be analyzed reliably with the IC method because of the organic interferences discussed earlier.

Figure 35 shows that water soluble Cl concentrations in the MHF tissues display a random distribution. Elevated concentrations occur mainly at the northern, less well drained end of the survey area. However, the highest concentrations (546 and 547 ppm) both overlie well-drained colluvial soils 200 metres up-slope from the alpine bogs. One of these samples (#776) lies close to the up-slope NE limit of the breccia zone but this is likely fortuitous. Values are slightly enriched near to the alpine bogs at the NNW end of the eastern and western lines but not on the original central sample traverse. Uniformly low values typify the central parts of the sampled area and there is no recognizable response to either mineralized zone.

Patterns are quite different between the ashed and non-ashed results (Figs. 32 and 35). In the ashed results (Fig. 32), concentrations are approximately four times higher than the non-ashed values, indicating that the ashing procedure frees Cl from tightly bound sites in the plant tissues and makes it available to leach in water soluble form. This change in Cl solubility appears to reveal the exogenic signal related to the breccia zone mineralization. Why this should be the case is not understood but could one of the subjects of future investigations. Of note is that some of the Cl was lost during ashing, because if all was retained, the Cl values in ash should be approximately 20 times higher (i.e. ~5% ash yield). This begs the question as to what Cl compound is retained – a question out of the scope of this project, but worthy of further research.



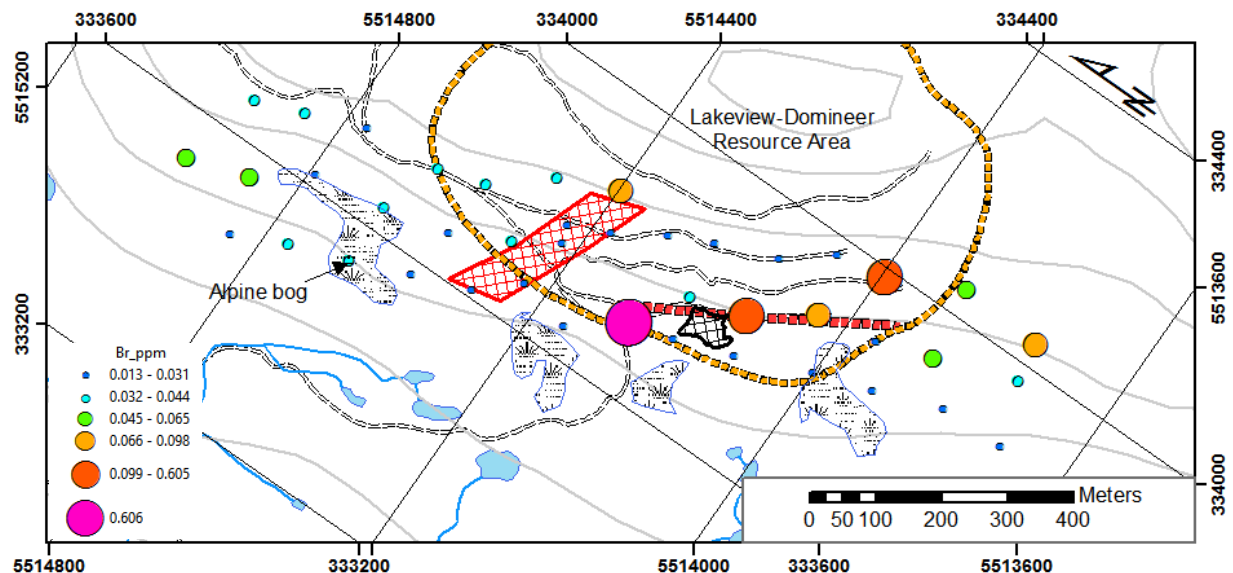
**Figure 35:** Chlorine H<sub>2</sub>O leach of milled MHF foliage.

Bromine patterns are also quite different between the two preparation methods. Figure 36 shows that elevated Br concentrations in the milled tissues are limited to the SSE end of the central and eastern sample lines with most of the anomalous values occurring along the Domineer vein trend. The maximum concentration (0.606 ppm) occurs at sample site 763, which lies downslope from the forest clearing containing the mine waste and ore stockpile. Mineralized boulders were noted just upslope from the sample site and therefore the possibility of contamination is quite likely for this response. There is no Br response over the breccia zone mineralization.

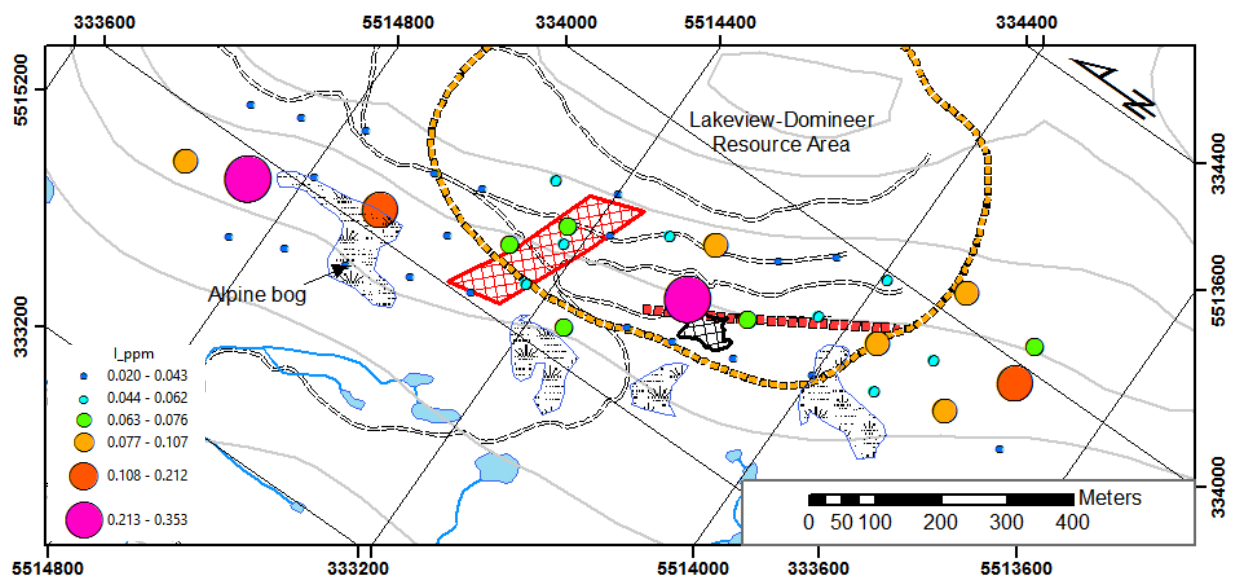
When compared to the ashed results (Fig. 33), the overall concentrations in the milled tissues are about two orders of magnitude lower than in the ashed samples. Again, this shows that ashing procedure releases tightly bound Br and converts it into a water-soluble form. Despite the much higher concentrations in the ashed samples, the contrast of the results is lower. Similar expressions of the Domineer vein trend are present in ashed results but the patterns are subtler. Moreover, the ash values do reveal a response, albeit a subtle one, over the breccia zone. This is not apparent in the milled tissue results.

Iodine patterns are less coherent. Figure 37 shows that this element has a random scatter of values across the sample lines with no recognizable patterns over either mineralized zone. The highest concentration (0.353 ppm) occurs at sample 740, which lies on the NW end of the

Domineer vein trend. However, elevated values of almost the same concentration are scattered at the SSE end of the survey and adjacent to the alpine bogs at the NNW end of the original sample traverse. In contrast, the ashed values (Fig. 34) display a coherent anomalous response over both mineralized zones. Once again, these results show that the ashing procedure somehow unlocks the exogenic response from the plant tissues. Interestingly the ashed concentrations are little changed from those of the milled tissue indicating that I loss during ashing is minimal.



**Figure 36:** Bromine H<sub>2</sub>O leach of milled MHF foliage.

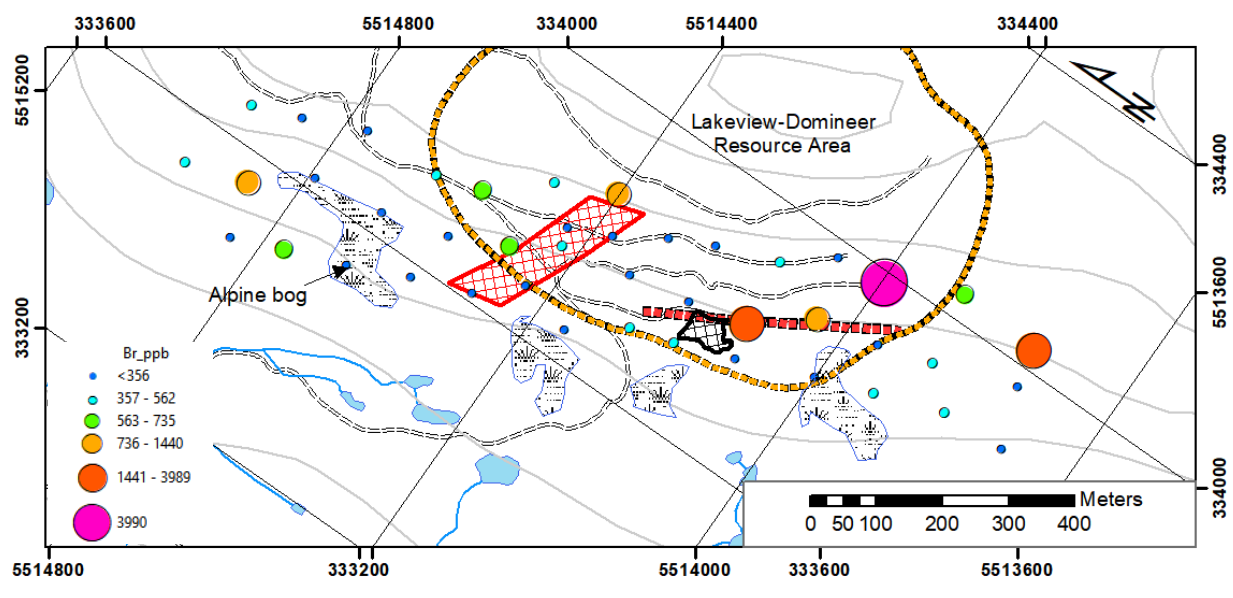


**Figure 37:** Iodine H<sub>2</sub>O leach of milled MHF foliage.

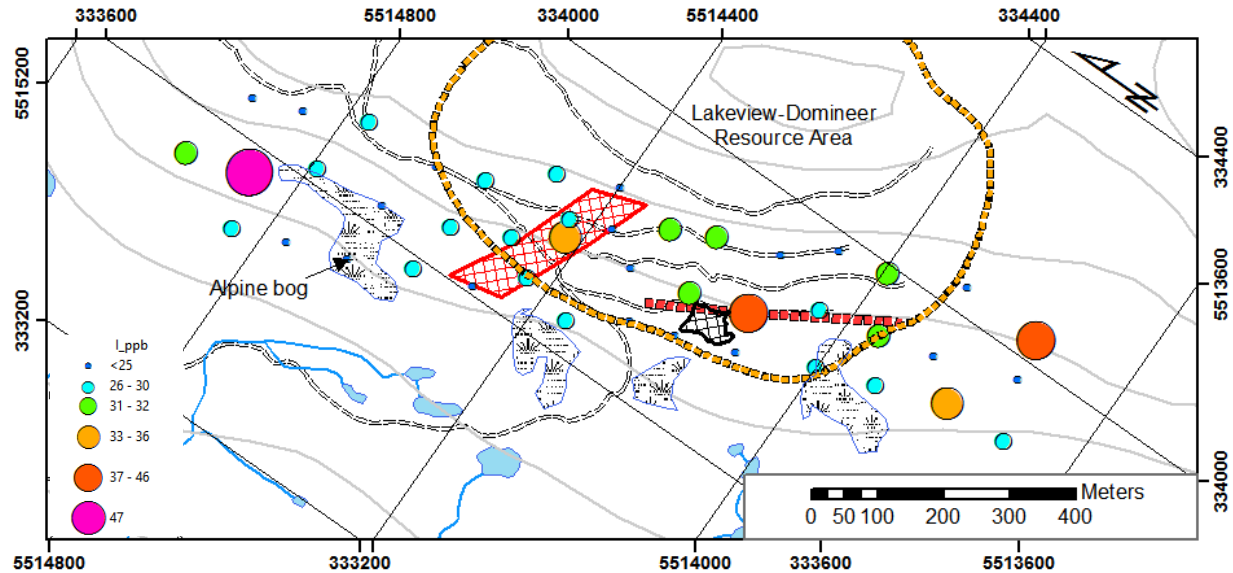
### Bioleach Br and I in mountain hemlock foliage

Bioleach Br results are shown in Figure 37. Values display very little contrast over the central and northern parts of the survey where concentrations are mostly at background levels (<356 ppb). The breccia zone does not have a convincing Br anomaly, although three samples on the SE and NW sides display values slightly above background. There is a more robust response along the Domineer vein trend where three weakly to strongly anomalous values lie on or slightly upslope from the inferred surface trace of the vein.

Figure 38 shows that the Bioleach I patterns are less coherent. As observed for Br, much of the central and northern parts of the survey area have values at or close to the background concentrations (<30 ppb). One exception is a strongly anomalous sample on the central transect near to the NNW limit of sampling. This sample has the highest I concentration of the survey (47 ppb); the reason for this is unknown. A single weakly anomalous value marks the position of the breccia zone. As it is surrounded by samples with background concentrations, it is difficult to assign too much significance to this response. Elevated concentrations also occur over the SSE part of the survey area, SE of the breccia zone. Iodine results do not have coherent patterns and appear to be randomly distributed across the sample lines. The two samples with the highest concentrations align along the Domineer vein trend but are separated by several samples with background values. It cannot be concluded that this is an expression of the mineralization and may just be an expression of elevated background conditions in hemlocks growing on well-drained colluvial soils. It must be concluded that Bioleach on MHF does not seem to be a reliable indicator of halogens associated with the zones of epithermal mineralization.



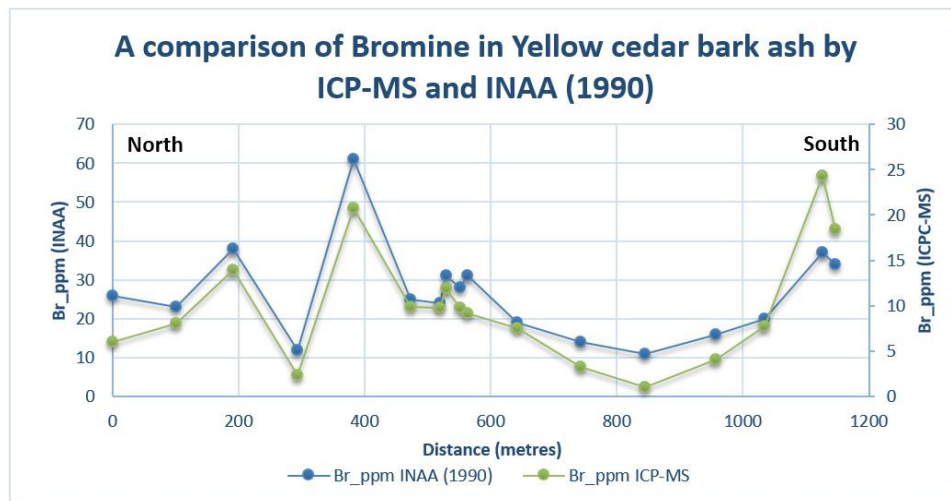
**Figure 38:** Bromine in MHF Bioleach.



**Figure 39:** Iodine in MHF Bioleach.

## Yellow-cedar bark ash

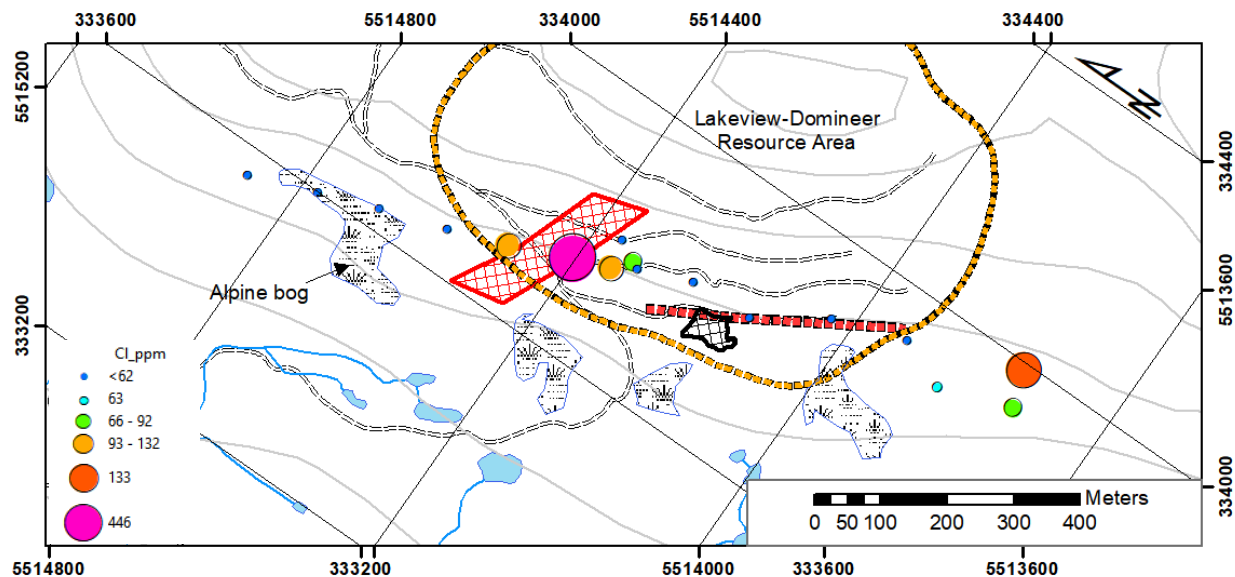
The second vegetation medium tested is yellow-cedar bark ash (YCB). The samples were originally collected and analyzed in 1990 by instrumental neutron activation (INAA). The INAA element suite included Br and this provides us a useful comparison with the ME-HAL01 method developed in this study. Figure 39 shows line profiles for Br for both methods. While individual samples have different concentrations for the two methods, the patterns are very consistent and suggest that the ME-HAL01 method is acceptably accurate for this element.



**Figure 40:** A comparison of Br in yellow-cedar bark ash by ICP-MS on a warm H<sub>2</sub>O leach and INAA (GSC, 1990).

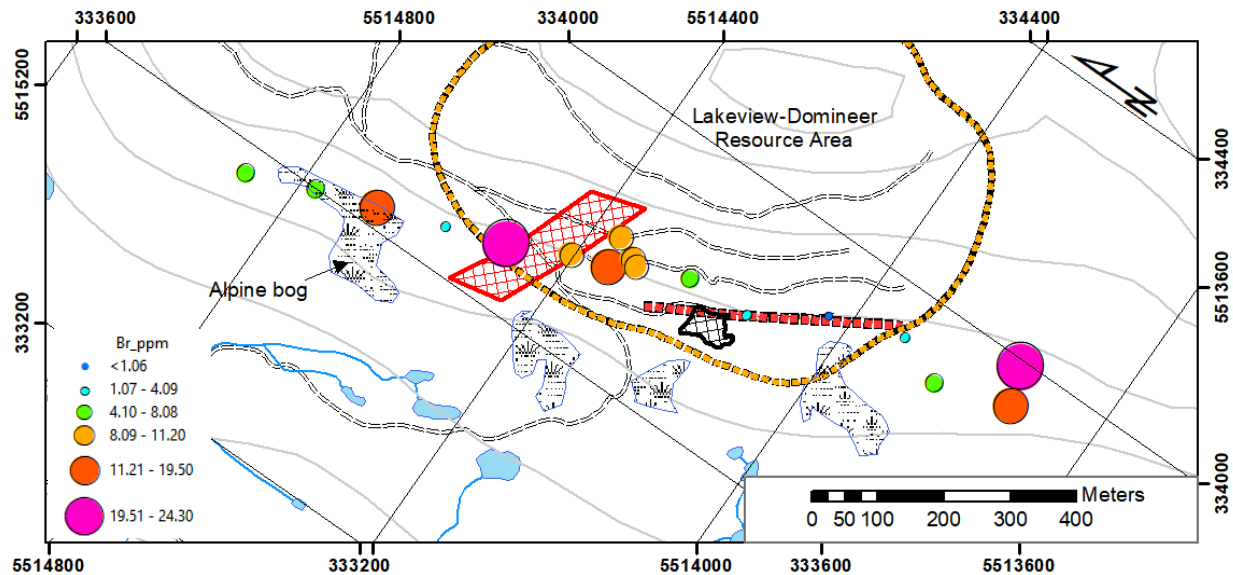
## Halogens in yellow-cedar bark ash (YCB)

IC F results were found to have unacceptable accuracy and precision to provide a meaningful interpretation. Figure 41 shows the Cl results for YCB ash. Most of the samples report values below the method detection limit (0.1 ppm) but elevated concentrations are present over the breccia zone where they form a moderately to strong three sample apical response. In addition, the two southernmost samples on the transect also have somewhat elevated Cl concentrations. Their location suggests that they may highlight the projected continuation of the Domineer vein trend.



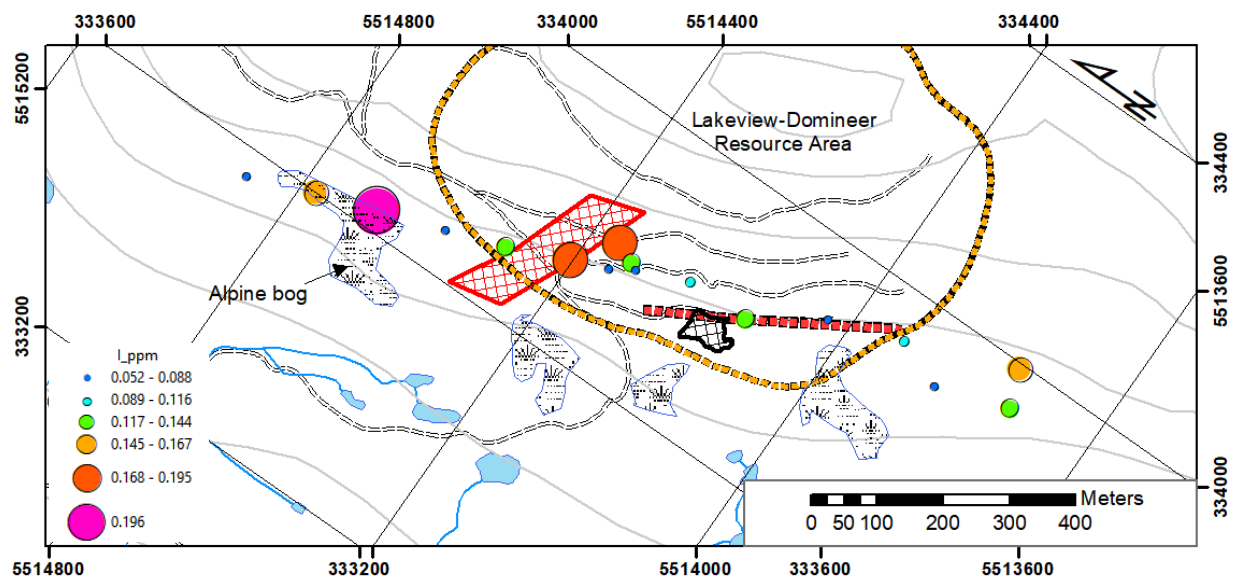
**Figure 41:** Chlorine in yellow-cedar bark ash.

Bromine results for the ME-HAL01 method are shown in Figure 42. Three areas with elevated values separated by background concentrations are present along the transect. At the breccia zone, Br is concentrated close to and just outside the inferred edges of the mineralization. A single highly anomalous value (20.8 ppm) lies on the NW side, and a cluster of five moderately anomalous values occur on the SE, producing what appears to be a rabbit-ear response. The maximum concentration (24.3 ppm) occurs at the southern end of the transect on the inferred Domineer vein trend continuation. It is accompanied by a second moderately anomalous sample. The two anomalous samples possibly indicate the presence of a mineralized structure in that area. The third anomaly is on the northern part of the line just up-slope from one of the alpine bogs. This area is anomalous in the Ah horizon samples as well and suggests that YCB may be more sensitive to soil halogen concentrations than the MHF.



**Figure 42:** Bromine in yellow-cedar bark ash.

Iodine results (Fig. 43) are somewhat like Br and show two areas with elevated values. The breccia zone is marked by a pair of moderately anomalous samples located on the S side of the mineralized zone. They appear to define more of an apical response than a rabbit-ear pattern and this is consistent with I patterns observed in other media. Near the NNW end of the transect, two anomalous samples occur adjacent to an alpine bog. Again, as seen in the Br results, their presence appears to highlight a difference between the YCB and MHF responses and suggests that the former is sensitive to soil halogen concentrations while the latter responds more to bedrock concentrations. Iodine does not have a response over the Domineer vein trend, where values are close to background.

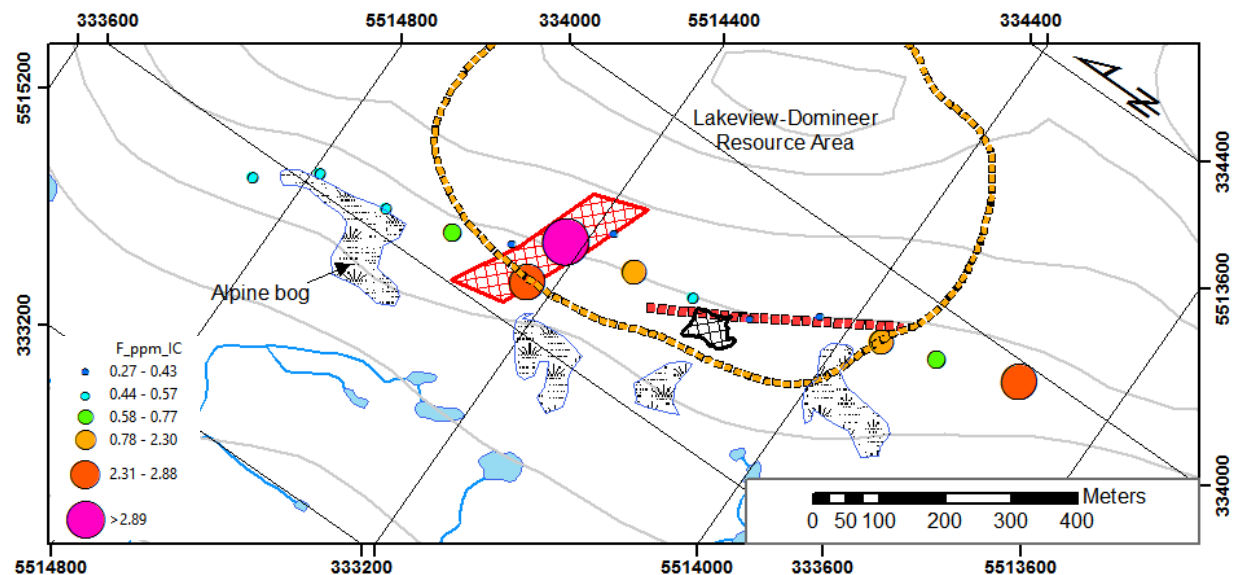


**Figure 43:** Iodine in yellow-cedar bark ash.

## *Halogens in Transpired Fluids*

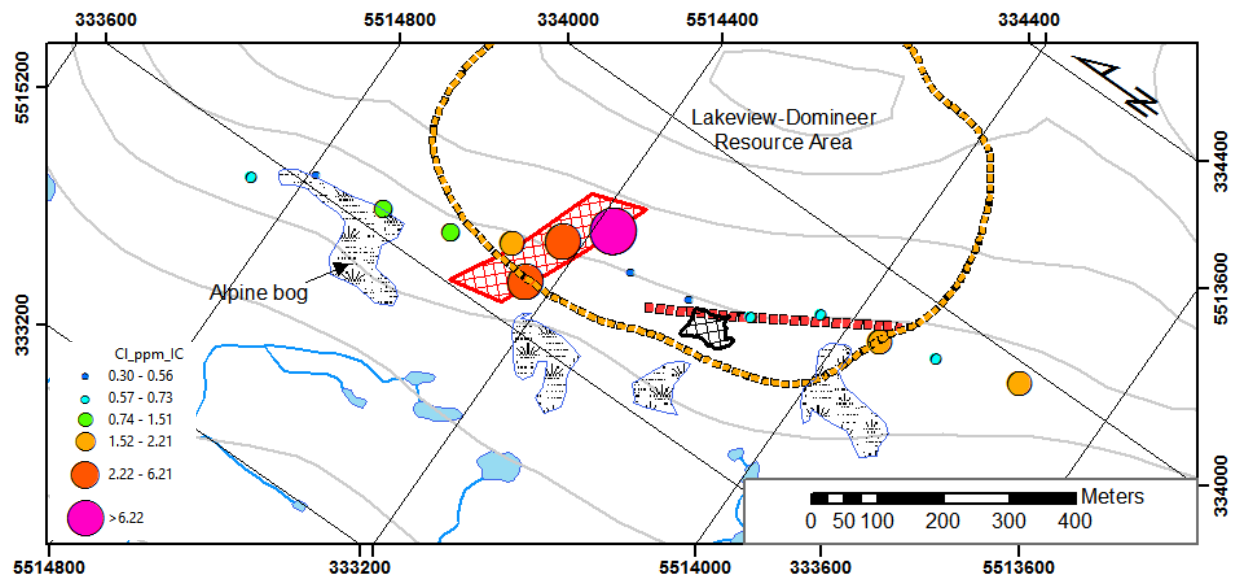
Transpired fluids provide perhaps the cleanest sample medium. Water evaporating from needle stomata has an unbroken connection through the tree's vascular system to the root-soil interface. As moisture evaporates at the extremities of the plant, more water is transported upwards through the xylem tissue by the cohesion-tension mechanism. Water absorbed from the soil through the root system should, if barrier mechanisms are absent, maintain the chemical characteristics of the pore waters. If these waters are in contact with altered or mineralized rocks, it is therefore reasonable to expect that some of the solutes derived from rocks will travel through the plant's vascular system to be transpired at its extremities. Some elements are extracted from the vascular system and used for metabolic processes, enzyme production and tissue growth, but others are either unconsumed or partially consumed and ultimately escape the tree. Thus, by directly sampling the fluids, a signature of the underlying bedrock may be identified. The results described in the following paragraphs refer to samples collected from Mountain hemlock twigs.

Fluorine concentrations in transpired fluids are presented in Figure 44. Two anomalous areas are apparent in the results. The most pronounced occurs over the breccia zone where two adjacent anomalous samples define a high contrast apical response directly on top of the mineralization. A third anomalous sample with a slightly lower concentration occurs 100 m to the SSE. Elevated values are also present at the SE end of the line along the projected Domineer vein trend. This anomaly is of lower contrast and is less continuous than the breccia zone response. Other media show halogen enrichment in the same area (e.g. Br and Cl in yellow cedar bark ash discussed above). Elsewhere on the line the transpired fluids contain only background concentrations (<0.56 ppm).



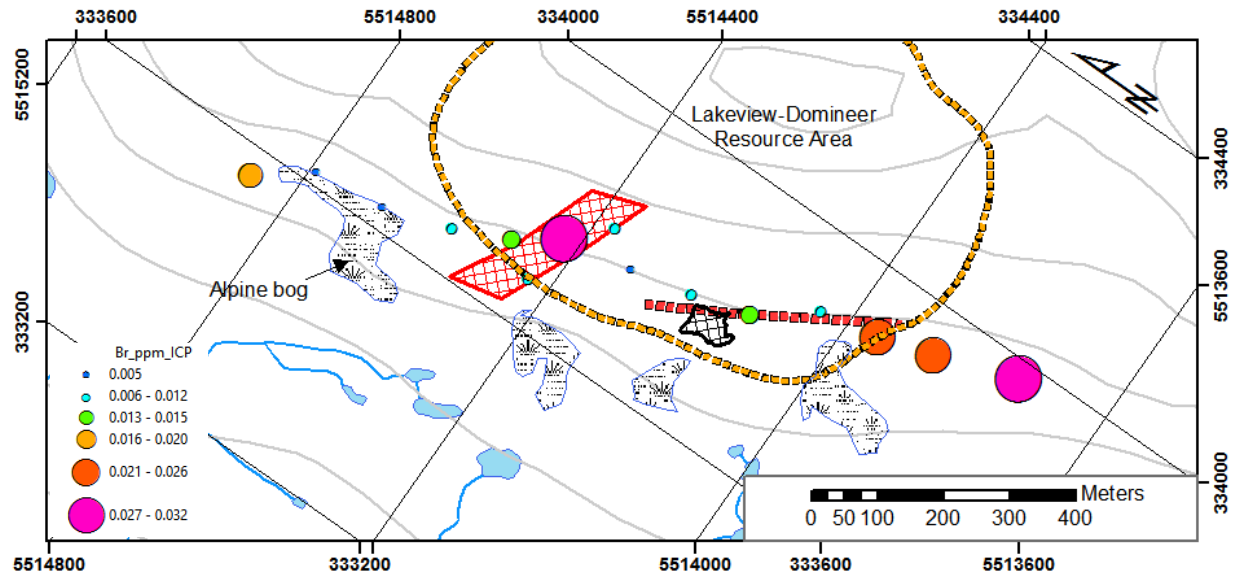
**Figure 44:** Fluorine in transpired fluids.

Chlorine also shows a strong apical response over the breccia zone consisting of four adjacent anomalous samples (Fig. 45). Within the anomaly, concentrations exceed 1.3 ppm and reach a maximum of 7.0 ppm at the SE edge of the zone. By comparison, background values at the NNW end of the line vary between 0.3 and 0.7 ppm. At the SSE end of the line, the Domineer vein trend has two samples with slightly elevated concentrations. They are separated by background values.



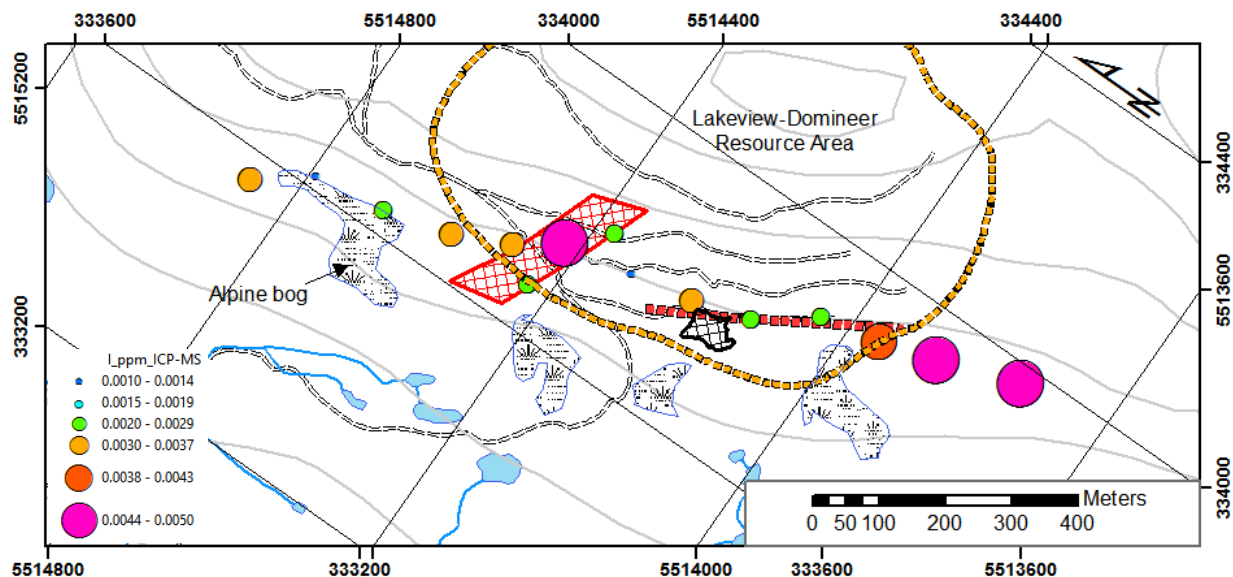
**Figure 45:** Chlorine in transpired fluids.

Somewhat different patterns are displayed by Br. Figure 46 shows that the strongest Br responses occur along the Domineer vein trend near the SE end of the line. Here, three contiguous anomalous samples display increasing concentrations towards the end of the line. In fact, the maximum concentration (0.032 ppm) occurs at the southernmost sample station (745). At the breccia zone, one sample (733) located directly over the mineralization has a strongly anomalous concentration, but other samples in this area contain mostly background values.



**Figure 46:** Bromine in transpired fluids.

Iodine results are shown in Figure 47. Concentrations display large variations from background to strongly anomalous along the sample line. The most anomalous areas are the breccia zone and the SSE end of the Domineer vein trend. The breccia zone is marked by a single strongly anomalous sample. This sample is flanked by two weakly anomalous responses immediately to the NNW. The three southernmost samples of the transect are also strongly anomalous for this element. The response is likely an expression of the vein system.



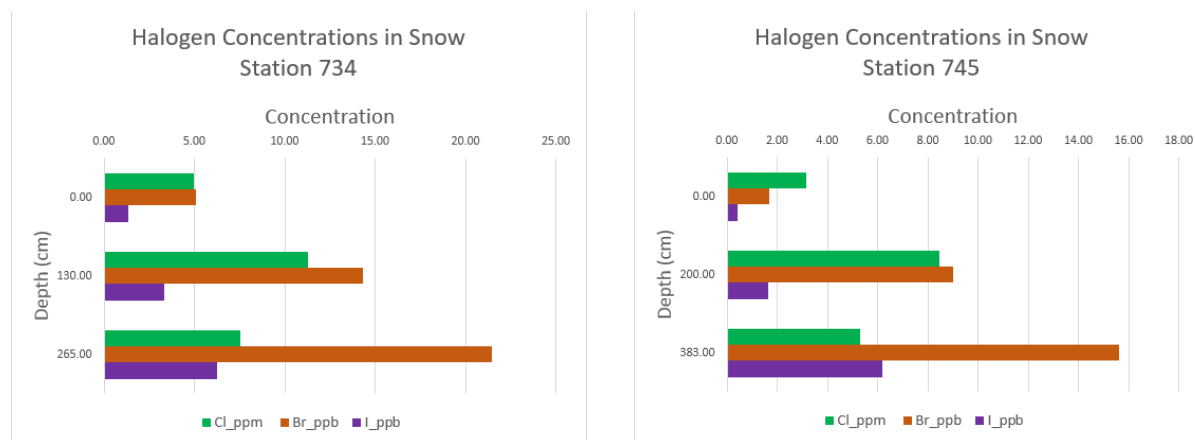
**Figure 47:** Iodine in transpired fluids.

## Halogens in Snow

Snow sampling was done to address two main questions:

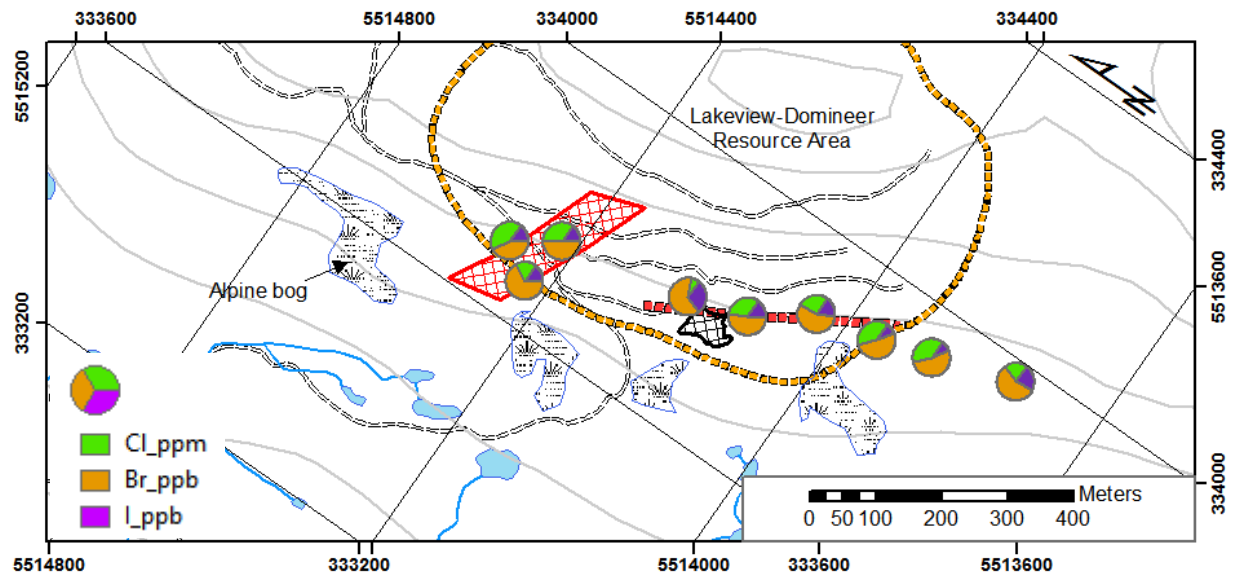
- 1) Is there a systematic variation in halogen concentrations from the base to the top of the snow pack that would indicate halogen flux from the ground; and
- 2) Is snow at mineralized stations more enriched in halogens, particularly at the ground surface, than snow at background locations?

To address the first question, snow was sampled at the base, middle and surface of the snow pack at two different stations (734 and 745). Figure 48 shows that there is a clear enrichment of Br and I at the base of the snow pack at each location with values diminishing progressively towards the surface. Bromine concentrations are 3 to 5 times higher than I in both profiles. Decreasing values from the base of the snow pack for both halogens indicate that there is a continual flux of these elements from the ground into the snow. Chlorine exhibits a relative enrichment in the middle of the snow pack at both locations. The reason for this is not clear but a strong possibility is that the enrichment is caused by leaching and downward percolation of atmospherically derived Cl (i.e. in precipitation).



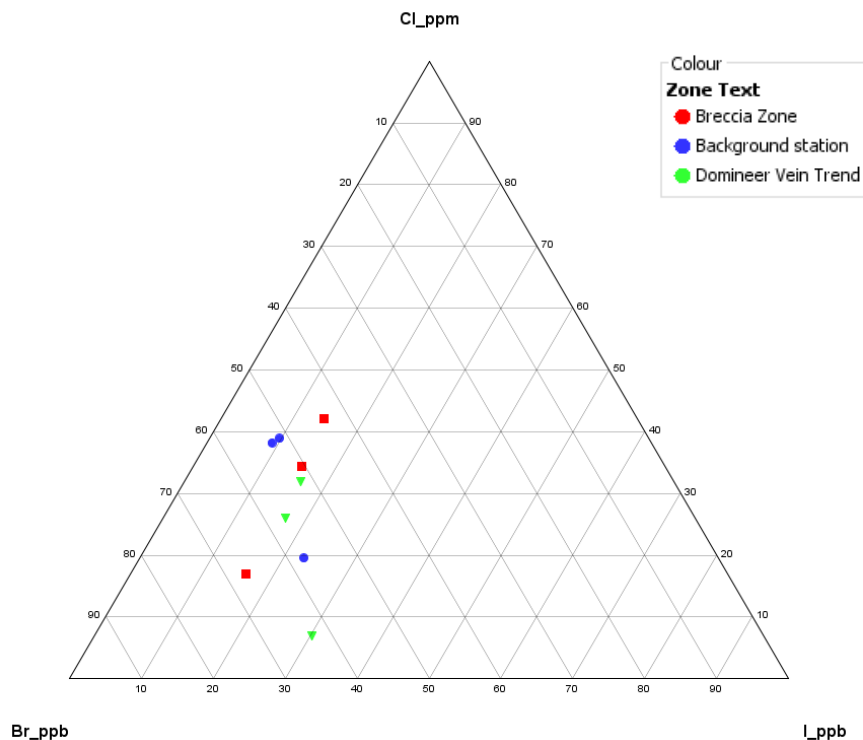
**Figure 48. Changes in halogen concentrations from the base to top of the snow pack.**

Spatial patterns along the transect are less clear. Figure 49 shows the variations in the relative halogen concentrations at each station presented as pie diagrams. Note that Br and I concentrations are in ppb and Cl is in ppm. Most of the samples display similar relative abundances of the three halogens. Bromine appears to be the most enriched accounting for over 50% of the pie area in the majority of samples. Iodine is relatively more enriched at station 740, located at the NNW end of the Domineer vein trend as well as at station 745 at the SSE end of the sample transect. Halogens are elevated in other media at this site (see previous discussions) however the cause of this enrichment has not been determined. There does not appear to be any obvious differences in the relative halogen abundances between the breccia zone and other locations.



**Figure 49.** Variations in Cl, Br and I in snow samples over the sample traverse. Bromine and I are in ppb and Cl values are in ppm.

A ternary plot of the snow results (Fig. 50) shows that all samples plot within a relatively small area of the diagram. There is no obvious separation between the breccia zone, the Domineer vein trend and background stations. From this result, it must be concluded that snow is not an effective medium for discriminating the position of mineralization. As a cautionary note, it must be appreciated that results in the section are based upon a very small sample population so should be considered as a first attempt to establish distribution patterns.



**Figure 50.** A ternary plot showing relative Cl, Br and I concentrations in snow samples. Note Bromine and I values are in ppb and Cl values are in ppm.

## Discussion

### *Fluorine Analysis*

One of the observations from Dunn et al.'s 2007 study was that misleading results could be obtained for F when analyzed by ion chromatography. While results could at first glance appear to produce meaningful signatures, it was apparent on further investigation that the presence of organic compounds in the water leach solutions can cause an interference with the F peak resulting in unrealistically high concentrations. For instance, warm water leach analysis of dried vegetation samples returned values more than 1000 ppm F when analysis by other methods returned concentrations close to detection limit (Dunn et al., 2007; Table 3). In fact, an important observation from that study was that significant differences in F concentration are produced by different analytical methods.

### Organic and Cl interferences

This study aimed to address this issue by eliminating the organic compounds from the water leach solutions. Several different methods were tried, including: oxidation with nitric acid, oxidation with hydrogen peroxide and removal of the organics by cooking and eventually ashing before water leaching. Addition of small quantities of nitric acid or hydrogen peroxide did successfully eliminate the organic compounds from the solutions but at the same time these oxidants produced new interferences with F from nitrate and hydroxyl peaks.

Ashing of the samples and then leaching with warm water proved to be the most effective method for F analysis by IC. Ion chromatography was chosen over ISE because of its potentially lower detection limits. The high ashing temperature (485°C) undoubtedly causes partial volatilization of F, however it was found that sufficient remained in the samples to be measured. Fluorine analyses produced by this method proved to have good precision but questionable accuracy. Therefore, we must conclude that further work is necessary to refine the IC method so make suitable for the determination of F in organic and/or Cl-rich samples. Nevertheless, reasonably precise and accurate results may be obtained from less organic rich media after ashing at 485 °C.

Another complication of the IC method for F is an interference observed in high Cl samples. The wide shoulder of the Cl peak can overlap and mask the subtler F peak on the chromatogram, resulting in below detection limit concentrations. This effect can be corrected for to some extent by carefully applying a Cl correction but the resulting values must be considered as semi-quantitative at best. Above a certain Cl concentration (still under investigation by ALS at the time of writing), samples would be deemed unanalyzable by IC.

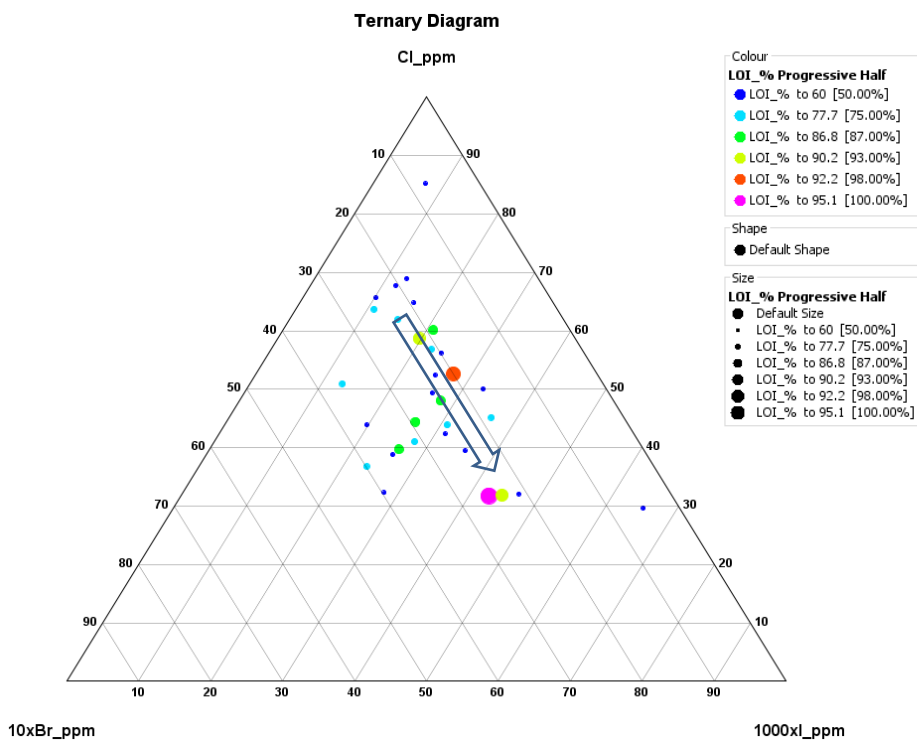
## Accuracy and Precision

One of limitations on the accuracy of the F analyses was the lack of well characterized standards. Control samples inserted in the field are the same as those used at the laboratory. Standard V14 is a custom-made standard that was prepared at BC Ministry of Forests laboratories (now BC Ministry of Environment) from mountain hemlock needles collected from Mount Washington by the second author in 2002. While concentration ranges for Au and some pathfinder elements are well characterized in both milled and ashed material, there are no data available on its halogen concentrations. Halogen analyses of V14 presented in this report represent the first determinations for this control. Therefore, the control can only be used as a drift and inter batch shift monitor. Unfortunately, the F results for V14 show large concentration differences between batches for the ME-HAL01 method.

## *Controls on halogen concentrations in soils*

Halogen results for the Ah horizon samples show a clear relationship with the amount of organic matter and the degree of water saturation of the soil profile. Chlorine, Br and I all show positive correlations with LOI (Fig. 10) but F does not appear to have a similar relationship. The lack of a correlation between LOI and F may be attributable to the poor precision of the F results. An important observation from the Ah horizon results is that the effect of organic matter overwhelms any exogenic signal that might be present from any underlying mineralization.

The observation that the halogens are concentrated with organic matter is consistent with the results of other recent studies. Beister et al. (2004) demonstrated that peat bogs are important sinks for halogens where they are retained as organo-halogen compounds. In their study of Chilean peat bogs, the halogen input was interpreted to be from atmospheric sources including precipitation and possibly oceanic aerosols. Net accumulation and retention of halogens was determined to be due to an imbalance between halogen loss from the deeper portions of the bogs (by water flushing) and atmospheric input and retention at the top (20 cm) of the profile. Beister et al. attribute organo-halogen enrichment to peat degradation/decomposition. They noted that Cl/Br ratios decrease (i.e. Br concentrations relatively increases) during the peat humification process. A similar mechanism is most likely operating in the alpine bogs at Mount Washington. A ternary diagram of Cl-Br-I (Fig. 51) in Ah horizon soil appears to show that there is a crude decrease in the Cl content with increasing LOI, possibly indicating Cl leaching and Br-I concentration as organo-halogen compounds. Figure 49 also shows that the Br/I ratio remains relatively unchanged.

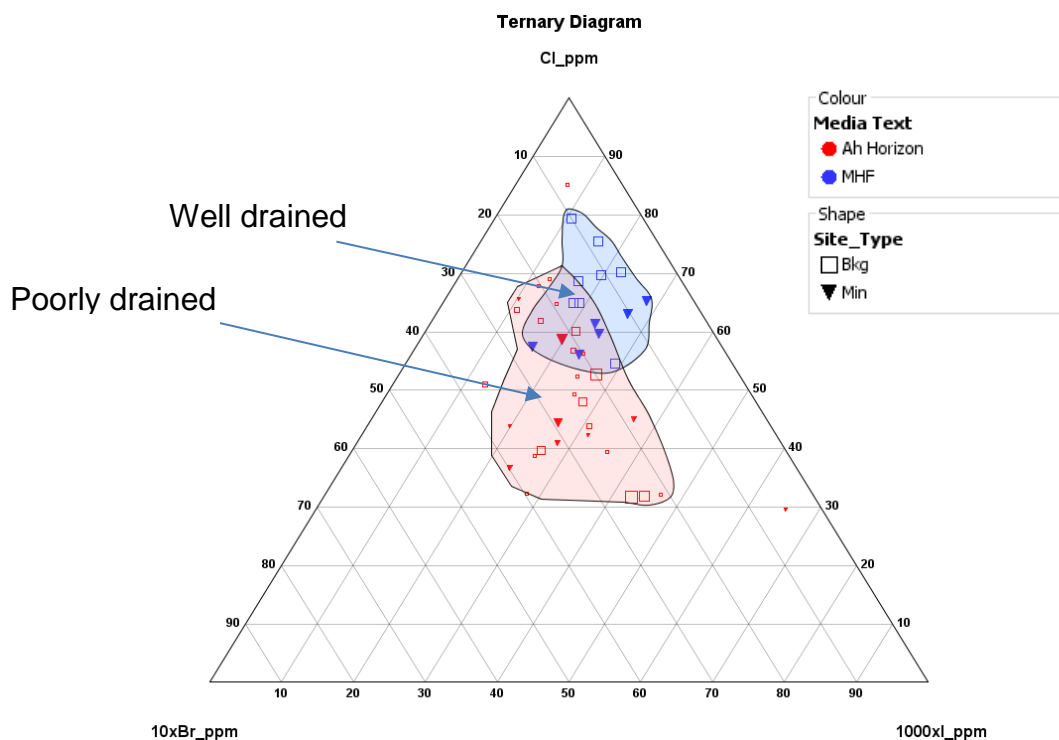


**Figure 51:** Cl-Br-I variations as a function of LOI in Ah horizon soils.

Halogen accumulation in Ah horizon in well-drained soils may follow the same mechanism to some extent with precipitation and possibly ocean derived aerosols being contributors. However, a study carried out by Öberg and Grøn in northern Denmark in 1998 demonstrated that a significant contribution to the total halogen content of the soil comes from needle litterfall from conifers, in that case from spruce trees. It is thus reasonable to assume that a similar process is happening at Mount Washington with the litterfall of mountain hemlock needles contributing to the halogen content of the Ah horizon. This could explain the generally higher Cl contents of the low LOI soils (Fig. 10). Figure 52 shows the Cl-Br-I contents of the MHF samples superimposed on the Ah results; symbol sizes are scaled by LOI %. The overlap between the MHF Cl-Br-I

compositions (blue) and the Ah horizon in well-drained soils implies that the soil halogen composition is derived almost entirely from litterfall from the hemlocks whereas in poorly drained areas the Ah horizon halogen composition is more reflective of organo-halogen accumulation. The main difference between the two environments appears to be a relative depletion of Cl in the more waterlogged soils.

This observation could explain the relative effectiveness of the two media at detecting the mineralization. As discussed earlier, the Ah horizon produces no recognizable responses over the mineralized zones whereas MHF show convincing anomalies. Organo-halogen accumulation in the poorly drained soils appears to be overwhelming the subtler mineralized response. Mountain hemlocks seem to be less sensitive to this process and the halogen contents of their needles thus more accurately reflect the composition of the underlying bedrock.



**Figure 52:** Cl-Br-I variations MHF (blue) and Ah horizon soils (pink). Min – Mineralized stations (solid symbols); Bkg – Background stations (open symbols).

### ***Halogens in other sample media and implications for dispersion mechanisms***

Halogen concentrations for all the sample media are plotted on a Cl-Br-I ternary plot in Figure 53. The relationship between the halogen contents of Ah horizon soil and MHF is discussed in the previous section; however, Figure 53 also includes additional information about mineralized (solid symbols) versus background locations (open symbols). Mineralized sites for the MHF results (blue inverted triangles) fall within the general cluster of data points for that medium. They show a slight displacement towards the right from the background sites suggesting that the mineralized sites are slightly more enriched in I compared to Br.

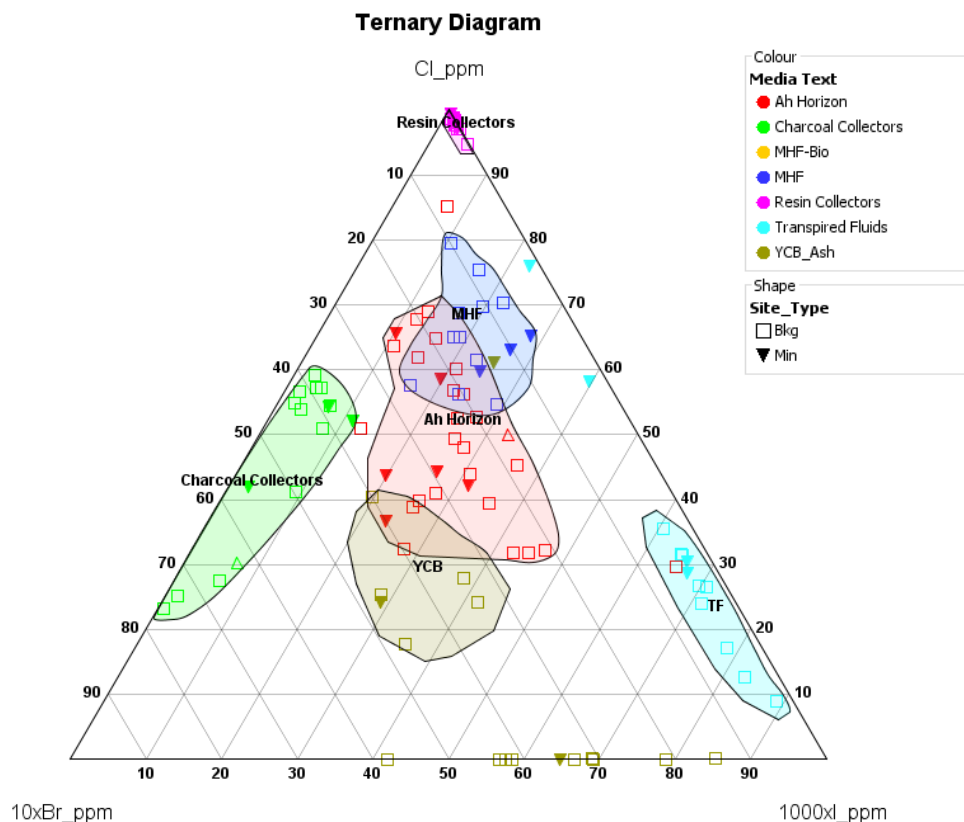
Mineralized sites for the Ah horizon samples (red inverted triangles) are distributed throughout the Ah field (pink polygon). Two occur near the top of the field in well drained soils with relatively high Cl concentrations and four occur near the bottom in relatively Cl depleted poorly drained soils. Ah horizon shows no consistent pattern differentiating mineralized from background sites confirming earlier observations that this medium does not detect the mineralized zones.

Yellow cedar bark (YCB) ash results fall along the same general trend defined by the MHF and Ah horizon soils. The trend indicates Cl depletion towards the bottom of the diagram but with a relatively consistent Br/I ratio. YCB has very low Cl contents, which may be because bark is a dead tissue and that Cl, being an essential nutrient, would be partitioned into the living tissues of the tree where it plays a key role in the operation of stomata as well as photosynthesis. Two samples of YCB collected over mineralization (olive inverted triangles) have very different halogen contents. One of them occurs within the YCB field and is indistinguishable from background sites; and the second plots within the MHF field demonstrating substantial Cl enrichment.

Transpired fluids (cyan symbols) all plot along the Cl-I axis showing that the fluids have very low relative Br concentrations. We know from analysis of its needles that mountain hemlock contains low levels of Br. Its absence from the transpired fluids therefore suggest that all the Br is being sequestered within the plant tissues and that none is being exuded in the transpired fluids. Mineralized sites (cyan inverted triangles) display a significant shift towards Cl along the Cl-I axis indicating that the transpired fluids from trees over mineralization have strongly elevated Cl concentrations.

Chlorine enrichment at the mineralized sites is also demonstrated in the charcoal ion collectors (green polygon). The ion collectors are designed to trap halogens emanating from the ground in vapour or gaseous form. Results for the charcoal collectors plot along the Cl-Br axis indicating an almost complete lack of I. Chlorine and Br are the most mobile of the halogens under surficial conditions while the heavier I tends to reside in the ground in immobile form as either organo-iodate compounds or to a much lesser extent inorganic forms adsorbed onto Fe and Mn hydroxides and clays (Shetaya et al., 2012). The lack of I on the charcoal collectors could be explained by the very slow flux of I ions emanating at the surface. In other words, the three months of burial was insufficient time to collect detectable levels of I on the charcoal collectors. Chlorine enrichment of the charcoal collectors is apparent at mineralized sites with two of the three mineralized sites sampled plotting at the high Cl end of the charcoal collector field.

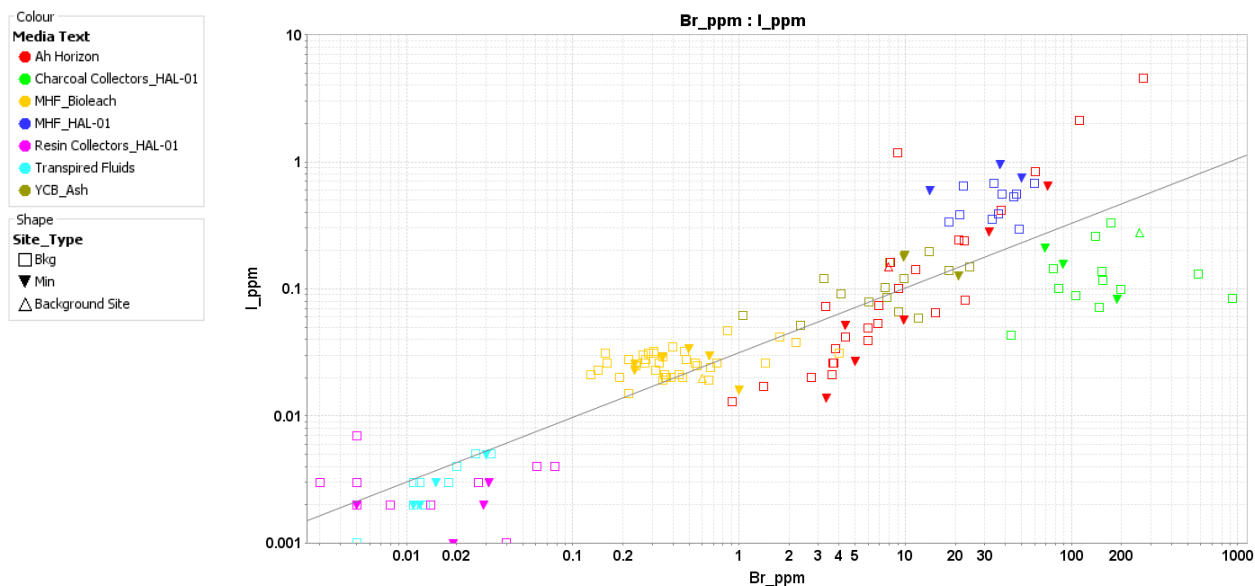
The resin collectors appear to be devoid of Br and I. All the analyses plot at the Cl apex at the top of the diagram. It is not known whether the resin material used was ineffective at capturing Br and I or whether it was extremely efficient at capturing Cl during the three months of burial. Therefore, it is difficult to extract meaningful conclusions from these results.



**Figure 53:** Cl-Br-I ternary plot for all sample media. Solid symbols indicate samples over mineralization; open symbols are background sites.

### ***Relationship between Br and I***

Figure 54 shows that MHF, Ah horizon and YCB have very similar Br:I ratios. This relationship is further investigated in a log-log scatter plot of Br versus I shown in Figure 54. This diagram reveals that all media plot close to the 10:1 Br:I ratio line. The diagram also shows that there is a large variation in halogen concentrations, particularly for Br, which spans almost five orders of magnitude while I concentrations span over three. Highest absolute concentrations are present in the charcoal collectors (Table 8).



**Figure 54:** Log scatter plot of Br vs. I for all sample media.

Ah horizon shows the greatest variation in Br concentration, spanning almost two orders of magnitude. The mineralized sample locations (solid symbols) are dispersed throughout the Ah field indicating that there is no systematic variation in the Br or I concentrations between mineralized and background locations.

Highest concentrations in natural media are in the MHF. This tissue displays a slight enrichment of I with respect to Br. In fact, the mineralized sites have generally higher I concentrations than the background site, implying that I is a good indicator of mineralization in this medium. It should be noted that Bioleach was carried out on powdered dry sample and that ME-HAL01a was done on ash. This likely explains the difference in the concentrations of the halogens. The ashing process appears to convert halogens from non-extractable to extractable forms.

Lower halogen concentrations are present in the YCB ash, however the 10:1 Br:I ratio is maintained in this medium. Lower concentrations are attributed to the fact that the bark is a dead tissue that has reduced capacity to retain trace elements, and in fact possibly only traces of Br and I get sequestered in the bark, since they are essential elements for many species of plants and would therefore be utilized in the plant's metabolism. Mineralized sites appear to have somewhat elevated I concentrations compared to the background samples.

By far the lowest Br and I concentrations are present in the transpired fluids and resin collectors. Despite falling close to the method detection limit (i.e. <0.035 ppm Br and <0.006 ppm I), transpired fluid values define a tight cluster with a consistent Br:I ratio. Mineralized sites do not appear to be preferentially enriched in either of these elements. The resin collectors form an irregular shaped cluster aligned more or less parallel with the Br axis. Horizontal quantization of I values are caused by proximity to the detection limit indicating that resolution of meaningful patterns from this medium would be unrealistic.

In summary, Figure 54 shows that Br:I ratios are on average constant throughout the different media. Charcoal collectors are relatively more enriched in Br than I and concentrations are higher than the surrounding soils suggesting that the collectors have captured Br emanating from

the ground. MHF and YCB both display I enrichment at mineralized sites, which means that this element could be a useful pathfinder in vegetation samples.

## Conclusions and Recommendations.

The following conclusion can be made from the results of this study:

- 1) Measurable halogen signals occur in organic media over the epithermal mineralized zones at Mount Washington.
- 2) The strength and geometry of the signals varies between media and halogen elements. Some, like Cl and I, tend to display apical responses over mineralization, while Br forms rabbit-ear patterns.
- 3) Weakest responses occur in the soil Ah horizon where halogen patterns are strongly influenced by the amount of organic material present in the -80-mesh fraction. Over poorly drained organic-rich substrate, the subtle mineralization signal appears to be overwhelmed by the elevated background caused by the accumulation of organo-halogen compounds.
- 4) Highest contrast halogen responses occur in the media with the simplest matrices, for example transpired fluids and charcoal ion collectors.
- 5) Other volatile compounds like ammonium and sulphate have measurable responses over mineralization. Ammonium defines a sharp apical response over the breccia zone. These compounds could be useful as pathfinders if reasonable cost commercial analysis could be done.
- 6) Experimentation with ion collectors and snow sampling demonstrates that there is a measurable halogen flux from the ground. In charcoal collectors and the base of snow pack, bromine has the greatest concentration and produces the highest contrast responses of the halogens. The lack of an I response in these media may point to a much slower flux of this element and suggests that longer sampling times may be needed to produce a measurable I signal.
- 7) Robust responses can be achieved in vegetation. Results show that MHF is a preferable medium to YCB for the detection of subcropping mineralization. The former appears to express a bedrock signal, while the latter appears to reflect the halogen concentrations of the overlying soil profile and is thus influenced by organic content.
- 8) Determination of F by IC proved to be highly problematic for organic and Cl-rich samples. While a main objective of this study was to develop a method for the determination of F in organic media, we were unable to come up with a reliable procedure within the time and budget constraints of the study. More research is needed into developing effective low cost methods for F analysis in organic media that would be attractive to the mineral exploration community.
- 9) Based on the analytical complications for F discussed above, the F results for the organic-rich samples (Ah horizon, WHF or YCB) must be considered with caution. Results for the transpired fluids and charcoal collectors are however acceptable.
- 10) Results for the other halogens are reliable but demonstrate highly variable precision between media. The most precise results were obtained from the charcoal collectors.

- 11) Snow sampling demonstrated that there is a measurable flux of Br and I emanating from the ground into the base of the snow pack. Unfortunately, halogen concentrations in snow do not appear to identify the positions of the mineralized zones. This result could be biased by the very small number of snow samples and inadequate sampling in background locations.
- 12) Analytical accuracy could not be assessed because of the control samples used are not characterized for halogen concentrations or certified for the methods employed. At best the results could be monitored for consistency using ‘nominal’ concentrations determined from repeated analyses of the materials.
- 13) For future exploration surveys in similar environments, either transpired fluids or MHF are the recommended media to collect. Charcoal collectors are also effective but require at least 3 months of burial. This could make their use unattractive to an exploration company.

## **Recommendations**

This project demonstrates that halogens may be used as pathfinder elements for the exploration for blind or subcropping mineral deposits. It also highlights the appropriate sample media and analytical methods to use. However, these are specific to one forest type and surficial environment and do not encompass all potential environments in BC. More work is needed to optimize sample media in other common forest types; for example, in the spruce, lodgepole pine or Douglas-fir forests of the interior.

Further development of the analytical methods is important if halogens are to become widely used by the mineral exploration community. Work should include further research into low detection limit methods for determining F in organic media. This should include further development of the IC method with the aim of eliminating interferences that affect the F chromatogram peaks, but should also include assessment of alternative approaches like electro-thermal volatilization-ICP-MS (ETV-ICP-AES) and pyrohydrolysis.

Another aspect for improving analytical quality would be the creation and certification of appropriate controls. Some suitable controls already exist but they require proper characterization to determine their total and water-soluble halogen contents on both dry and ashed material. Collection and certification of new control samples is necessary for other common tree and understorey species found throughout BC.

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