Seaweed as an exploration medium along inlets on the west coast of Canada. Part 1: Methods and results from Jervis Inlet

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Seaweeds are marine macroalgae of which more than 40,000 species are known (Vinogradov 1953); approximately 650 species are found in northeast Pacific ocean waters (Gabrielson et al. 2000). They can be classified into three main groups according to their habitat and colour: 1) green seaweeds (Class Chlorophyceae), mostly from the upper tidal zone; 2) brown seaweeds (Class Phaeophyceae), mostly in the mid-tidal zone; 3) red seaweeds (Class Rhodophyceae), mostly from the low tidal zone. Along the fjorded inlets of western Norway, Greenland and Canada, by far the most common seaweeds in the intertidal zone are the brown rockweeds (*Fucus spp.*), also known as wrack or bladderwrack. Along the southwestern coast of British Columbia (BC), Canada the most common species is *Fucus gardneri* (Fig. 1). It grows to 40–50 cm with irregularly dichotomous branches and is attached, generally to rock, by a discoid holdfast. This holdfast is purely physical and does not access the composition of the underlying rock. Colour variation is from pale to dark yellowish green, getting darker as it dries out between tides. It commonly has pale olive air bubbles (bladders) near the frond tips.

1a

1b

1c

1d

Figure 1: Rockweed (*Fucus gardneri*) in intertidal zone off the south-east British Columbia coast and collecting samples for analysis.

Rockweed chemistry applied to mineral exploration and environmental monitoring

Various researchers have examined the chemical composition of rockweed, including general studies by Black & Mitchell (1952) and Bollinberg (1975); and local studies from Greenland (Bollingberg & Cooke 1985), Wales (Fuge & James 1973, 1974), Ireland (Cullinane & Whelan 1982), Sweden (Forsberg *et al*. 1988), England (Bryan & Hummerstone 1973; Morris &

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Bale 1975), Norway (Sharp & Bölviken 1979) and USA (Yang 1991). A comprehensive guide to seaweeds of BC is given by Scagel (1967).

Experimentation on the element absorption of rockweed and many other species of seaweed from the coast of southern BC, was conducted by the Geological Survey of Canada in the early 1990s (Dunn 1990; Dunn *et al*. 1993) and an overview published as a chapter in a book on metal hyperaccumulator plants (Dunn 1998).

The rugged coastline of BC with its steep cliffs into the mountainous hinterland and many incised streams that drain into the sea provide a challenge to mineral exploration. However, where streams cut into the rocks they inherit the chemical signature of those rocks. If a stream cuts through mineralization, the waters become slightly enriched in elements associated with such mineralization. The stream waters emerge into the sounds where their metal contents can be readily taken up in the nearby rockweed. With these principles in mind, a sampling program was devised to collect rockweed just seaward from where the streams meet the sea. The rationale being that if the seaweed is relatively enriched in a commodity metal (and/or its pathfinder elements) this would generate a focus for more detailed follow up into the mountains to look for the source – using other prospecting methods such as stream sediments, stream moss mats or the stream waters themselves.

To date, three areas have been sampled – along the shores of much of Jervis Inlet; around the shores of Texada Island; and around Howe Sound (Fig. 2). Samples from the latter area collected in 1990 included coastal areas down-drainage from the former Britannia Cu mine and were found to contain dramatically higher concentrations of Cu and Zn than samples from the same sites collected in 2015, attesting to the efficiency of the steady clean-up efforts over the past quarter century. This article deals with Jervis Inlet; subsequent articles will focus on the other areas at a later date.

Sample Collection and Analysis

A 45 foot ocean-going yacht gave relatively fast transport along the coast to the proposed sample sites. On approaching a planned sample station, a rubber 'Zodiac-style' boat with a 10 HP motor and a two-person crew launched from the moored yacht to the shore. A suitable site for collecting a seaweed sample such as a cliff face (Fig. 1, bottom right) or a flattish rocky promontory (or beach) was visually identified. Cutting the motor enabled the boat to drift up to the sample site, or (if needed) the crew to get on shore (Fig. 1, top left). A fresh sample weighing about 100 g was plucked from the rocks (avoiding the small holdfast structure at the base). Barnacles, mussels or other small shellfish were removed; the sample was placed in a Hubco "New Sentry" spun bound polyester sample bag (7" x 12.5"), and the drawstring pulled closed.

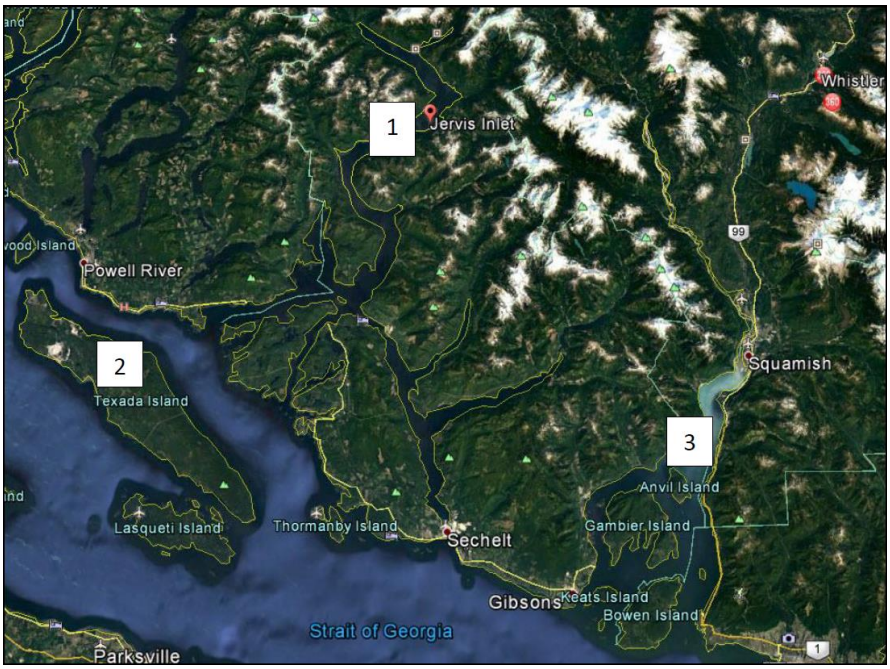

Figure 2: Survey areas - 1) Jervis Inlet; 2) Texada Island; 3) Howe Sound on the west coast of British Columbia (Google Map).

Samples were oven-dried at 80°C resulting in up to 80% mass reduction due to water loss with variation directly related to exposure time in sunshine between high-tides. Each dried sample was reduced to fine powder in a coffee mill prior to digestion of a 0.5 g aliquot in modified aqua regia (1:1:1 HCl – HNO_3 – H_2O) at 95°C for 1 hour and analysis by ICP-MS and ICP-ES for 65 elements (method VG101-EXT+REE at Acme Labs/Bureau Veritas, Vancouver). A separate aliquot was also reduced to ash by controlled ignition in a furnace held at 485°C for 16 hours and element concentrations determined by the same analytical methods (method VG104-EXT+REE). The ash yield from the dry material was 15-20% with the median and means both close to 16.5%.

Analytical results showed that the ashing process resulted in no loss of most elements; total volatilization of Hg, moderate losses (up to 30%) of As, Fe and Se and minor losses (<10%) of Cd, Cr, Ge, Sb and Sn. Nearly all samples reported below the method detection limits for Be, Bi, In, Nb, Pd, Pt, Ta, Th, Tl, W and most of the HREE. Precision on blind control samples was extremely good with RSDs better than 10% for all elements except those with concentrations close to detection levels (Au, Be, Ge, Hf, In, Re, Se, Te, W, Zr and some of the HREE). Pb in dry samples had 28% RSD, largely because of some drift in the analytical sequence. Precision of field and laboratory duplicates was similar to that obtained on the blind controls. Of relevance to this study is that the naturally higher Re in the field samples generated better precision than the lower concentration control samples. Concentrations referred to in the following text and plots are from the analysis of dry tissues, since the ashing did little to enhance distribution patterns and so was discontinued for the succeeding surveys.

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Location

The southern end of Jervis Inlet is located about 100 km northwest of Vancouver and snakes northward from Saltery Bay for 75 km (Fig. 3). There is road access as far as Earls Cove at the southern end of the Inlet, but no roads or trails extend farther to the north, requiring boat access.

Figure 3: Location of Jervis Inlet. Source Google Maps https://maps.google.ca

Geology

The lower Jervis Inlet area is in deeply dissected, mountainous country in which the main deep valleys have been invaded by the sea. For an extensive distance up the coast of British Columbia there is a system of inlets that penetrate the mountains for varying distances, resulting in typical fjords (Bacon 1957).

Bedrock is primarily Jurassic to Tertiary quartz-diorite and granodiorite of the Coast Plutonic Complex, overlain locally by basalts, andesites and volcaniclastic rocks and some Lower Cretaceous Gambier Group sediments. Quaternary deposits fill some valleys. For details of the bedrock geology map of British Columbia the reader is referred to http://www.geosciencebc.com/i/pdf/Maps/NVI/NVI-1-1_geology.pdf

Because of the extreme ruggedness, sometimes dense rainforest, and overburden of variable thickness, detail of the geology is poorly known, and to date little has been found to suggest that the granitic rocks of the survey area warrant further attention by prospectors. However, a few studies have shown that rocks of the Jervis Group contain small deposits of Cu, Zn, Pb and Au. Local occurrences of molybdenite are reported. Two adits into a small stock of gabbro-diorite on the west side of Upper Jervis Inlet intersected quartz veins and quartz-filled shear zones containing Au, Ag, Cu, Pb and Zn mineralization and a single 40 cm section yielded 0.72 oz/t Au with minor Co, Co and Bi (Laird 2008).

Seaweed (Rockweed [Fucus]) Survey

The Jervis Inlet survey was conducted in August of 2013. Samples were collected from 47 stations, mostly at intervals of 2-5 km along the shore, with additional samples where streams were seen draining into the sea. Including controls, a total of 60 samples were submitted for analysis. The 7 splits of a rockweed control sample showed that analytical precision was very good with RSDs mostly better than 10%, except for a few elements (e.g. heavy REEs, Au, Hg, and Ge) that had concentrations close to the detection limits of the analytical method, yielding RSDs mostly better than 30%. Similarly, the reproducibility of the field and laboratory duplicates varied from good to excellent for almost all elements.

Results

Table 1 summarizes the element concentrations in the 47 samples. Raw data are listed in a digital file (Appendix A) that is posted on the AAG website (https://www.appliedgeochemists.org/index.php/publications/explore-newsletter). Background

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Google Earth images on which the data are plotted in Figures 4, 5 and 6 are intentionally provided at low resolution in order to show the contrast between land mass and water. Most elements exhibit a fairly normal distribution, with a few outliers of which the more notable is a single sample yielding 83.8 ppb Au which is more than 2 orders of magnitude higher than the median. Analysis of the ashed sample confirmed that the Au is highly anomalous. Its source is unknown.

Table 1: Element concentrations in dry rockweed.

		D.L.	Min.	Mean	Median	Max.
Ag	ppb	2	13	26	23	63
Al	%	0.01	0.01	<0.01	<0.01	0.23
As	ppm	0.1	8.3	15.9	15.7	26.5
Au	ppb	0.2	0.2	3.0	0.7	83.8
B	ppm	1	50	87	86	121
Ba	ppm	0.1	8.7	13.6	12.6	30.4
Be	ppm	0.1	<0.1	<0.1	<0.1	<0.1
Bi	ppm	0.02	<0.02	<0.02	<0.02	0.05
Ca	%	0.01	0.72	1.32	1.32	2.59
Cd	ppm	0.01	1.1	1.7	1.7	3.02
Ce	ppm	0.01	0.04	0.12	0.07	1.24
Co	ppm	0.01	0.32	0.74	0.56	3.19
Cr	ppm	0.1	1.6	3.1	2.1	18.1
Cs	ppm	0.005	0.022	0.039	0.037	0.149
Cu	ppm	0.01	0.97	1.74	1.54	5.58
Dy	ppm	0.02	<0.02	<0.02	<0.02	0.13
Er	ppm	0.02	<0.02	<0.02	<0.02	0.08
Eu	ppm	0.02	<0.02	<0.02	<0.02	0.03
Fe	%	0.001	0.009	0.027	0.014	0.37
Ga	ppm	0.1	<0.1	<0.1	<0.1	0.6
Gd	ppm	0.02	<0.02	<0.02	<0.02	0.13
Ge	ppm	0.01	<0.01	<0.01	<0.01	0.08
Hf	ppm	0.001	<0.001	<0.001	<0.001	0.008
Hg	ppb	1	2	5.9	5.5	12
Ho	ppm	0.02	0.02	<0.02	<0.02	<0.02
In	ppm	0.02	<0.02	<0.02	<0.02	<0.02
K	%	0.01	1.34	2.03	2.04	2.76
La	ppm	0.01	0.03	0.08	0.06	0.6
Li	ppm	0.01	0.15	0.35	0.28	2.36
Lu	ppm	0.02	<0.02	<0.02	<0.02	<0.02
Mg	%	0.001	0.525	0.663	0.661	0.881
Mn	ppm	1	23	40	35	122
Mo	ppm	0.01	0.08	0.14	0.13	0.39

		D.L.	Min.	Mean	Median	Max.
Na	%	0.001	0.459	1.502	1.455	2.82
Nb	ppm	0.01	<0.01	<0.01	<0.01	0.21
Nd	ppm	0.02	0.02	0.08	0.06	0.65
Ni	ppm	0.1	2.7	4.2	3.6	11.6
P	%	0.001	0.054	0.087	0.083	0.138
Pb	ppm	0.01	<0.01	0.10	0.07	0.67
Pd	ppb	2	<2	<2	<2	3
Pr	ppm	0.02	<0.02	<0.02	<0.02	0.18
Pt	ppb	1	0	<1	<1	0
Rb	ppm	0.1	5.3	8.7	8.9	10.7
Re	ppb	1	2	18	18	43
S	%	0.01	1.2	1.72	1.67	2.59
Sb	ppm	0.02	0.06	0.13	0.12	0.24
Sc	ppm	0.1	0.1	0.2	0.2	0.6
Se	ppm	0.1	<0.1	0.3	0.3	0.5
Sm	ppm	0.02	<0.02	<0.02	<0.02	0.14
Sn	ppm	0.02	0.02	0.07	0.05	0.19
Sr	ppm	0.5	345	535	521	886
Ta	ppm	0.001	<0.001	<0.001	<0.001	0.003
Tb	ppm	0.02	<0.02	<0.02	<0.02	0.02
Te	ppm	0.02	<0.02	<0.02	<0.02	<0.02
Th	ppm	0.01	<0.01	<0.01	<0.01	0.13
Ti	ppm	1	<1	10	2	158
Tl	ppm	0.02	<0.02	<0.02	<0.02	0.02
Tm	ppm	0.02	<0.02	<0.02	<0.02	<0.02
U	ppm	0.01	0.49	0.9	0.9	1.66
V	ppm	2	<2	<2	<2	5
W	ppm	0.1	<0.1	<0.1	<0.1	<0.1
Y	ppm	0.001	0.056	0.132	0.102	0.749
Yb	ppm	0.02	0.02	<0.02	<0.02	0.06
Zn	ppm	0.1	9.1	18.3	16.5	46.5
Zr	ppm	0.01	0.06	0.11	0.10	0.24

Figure 4 shows that Ag and As are more concentrated toward the southern end of the inlet than in the northern arm suggesting a source of metal enrichment to the east – perhaps from the valley indicated.

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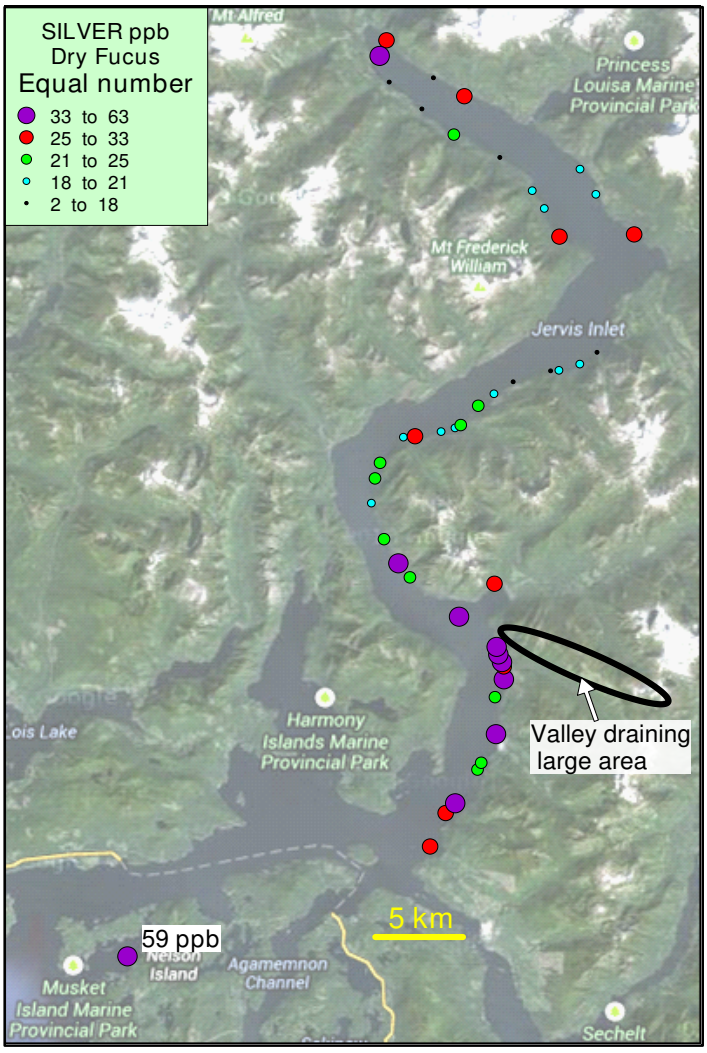

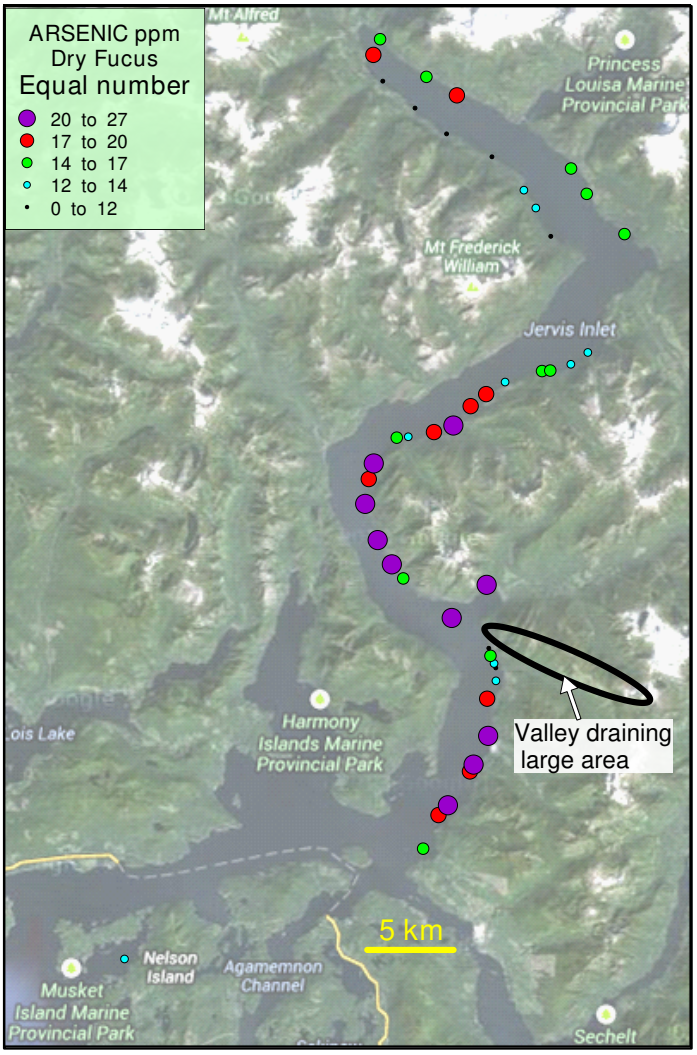

Figure 4: Ag and As contents in oven-dried rockweed determined by ICP-MS.

At the north end of the inlet, where there is an abundance of water and sediment draining from two large streams that extend to the north and northeast there is a relatively strong signature, compared to the rest of the inlet, of Cu, Mo, Ni, Co (Fig. 5) with associated Fe, REE and U suggesting a possible mineralized source upstream. Although the evidence is scant for predicting the type of mineralization, a similar suite of elements occurs in iron oxide copper gold (IOCG) deposits. However, Au levels are low in the seaweed from this area. The other area of relative enrichment is in the south, coincident with sites of Ag and As enrichment south of the valley indicated on Fig. 4.

Rhenium concentrations in vegetation are typically <1 ppb Re, but in brown seaweed they can be much higher. High enrichments (thousand-fold) of Re relative to seawater have been reported along the California coast, and it was concluded that brown algae acts as a biological sink of Re in oceans (Yang 1991). The highest concentrations of Re (up to 43 ppb Re) are at the southern end of Jervis Inlet. It is surmised that a higher concentration of fresh water from stream meltwaters draining from the mountains in the northern part of the inlet results in stratification of fresh water over the denser seawater. The similar distribution pattern shown by Na is further indication that the northern waters are less saline than those to the south. Similar patterns are exhibited by S and K.

Summary and Conclusions

The brown rockweed *Fucus* grows in abundance in the intertidal zones of the northwest shores of Canada and the USA, and is easy to collect by boat. Where a stream flows over or through mineralized bedrock, the waters can become slightly enriched in elements associated with such mineralization, and many streams emerge into the sounds where their metal signatures can be readily detected in the rockweed close by. Seaweed anomalously enriched in a commodity metal (and/or its pathfinder elements) can provide focus for a more detailed follow up into the mountains to look for the source – using other prospecting methods such as stream sediments, stream moss mats or the stream waters themselves.

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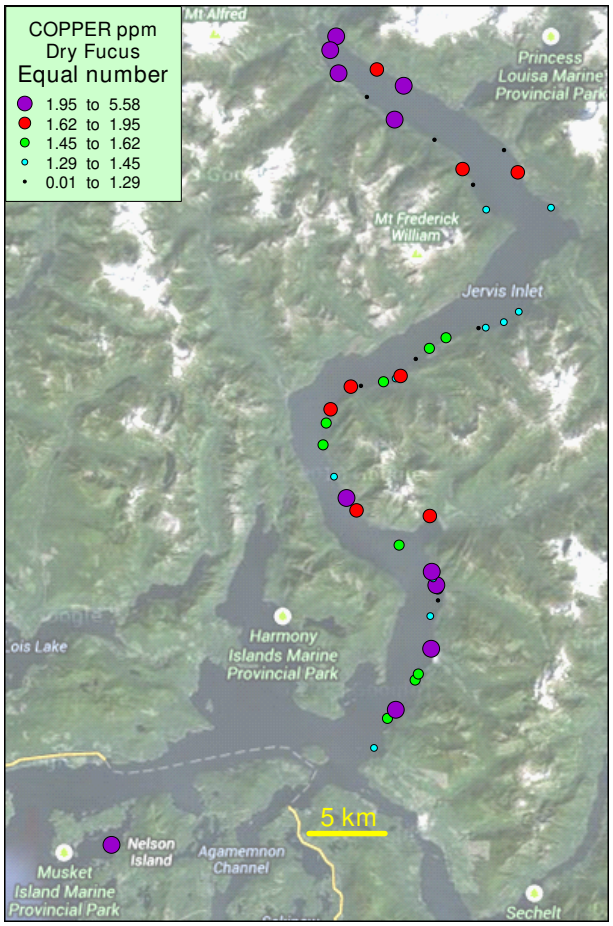


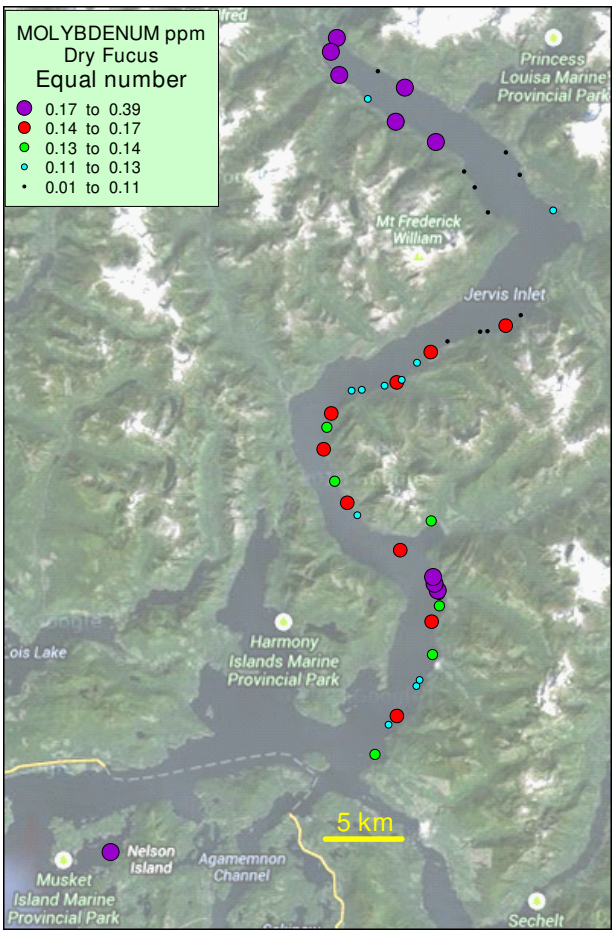
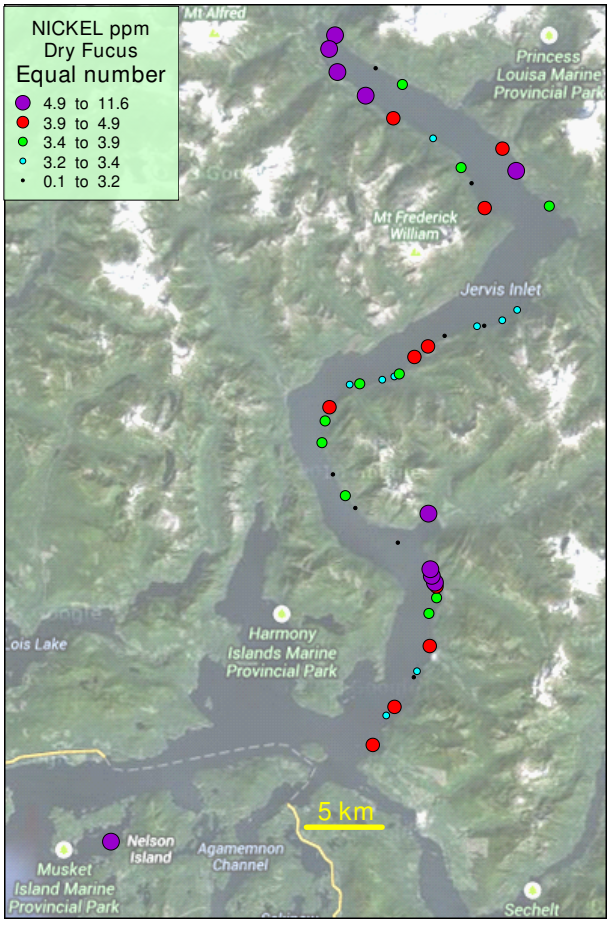


Figure 5: Cu, Mo, Ni and Co in oven-dried rockweed determined by ICP-MS.



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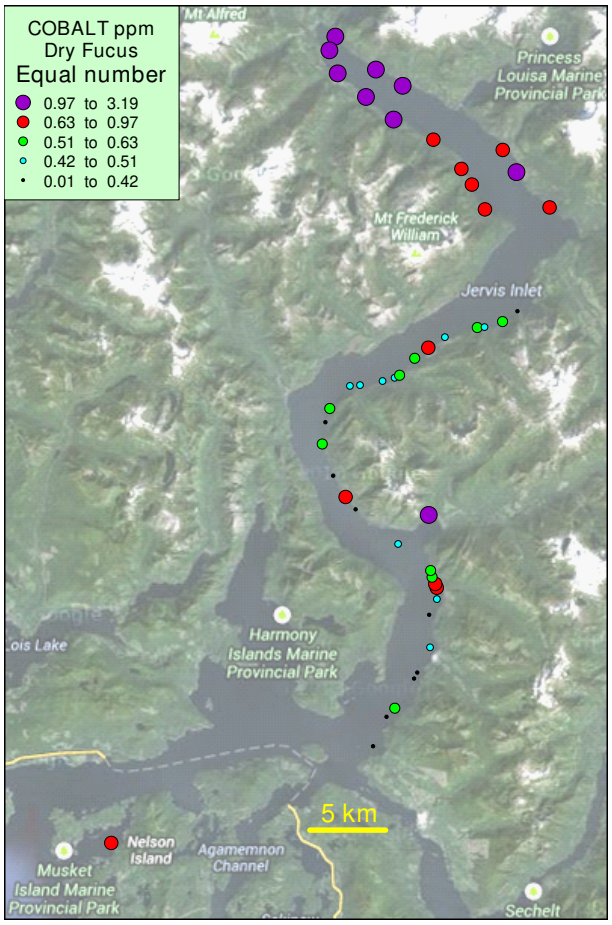

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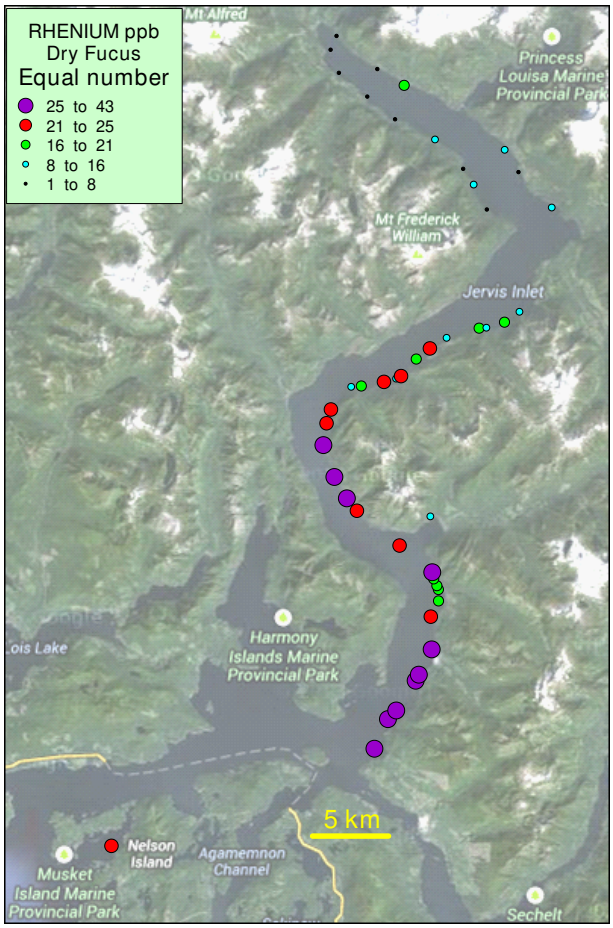


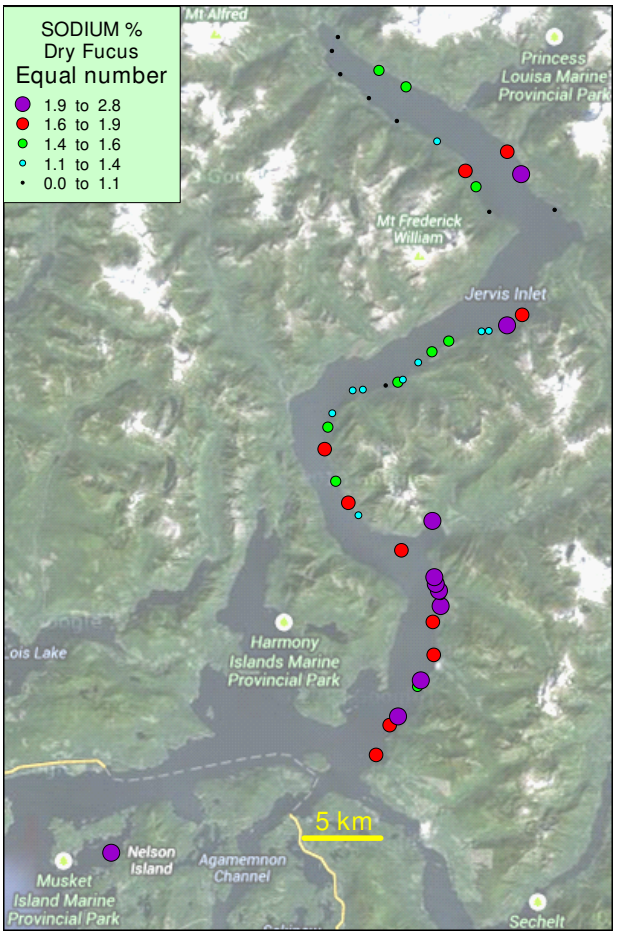
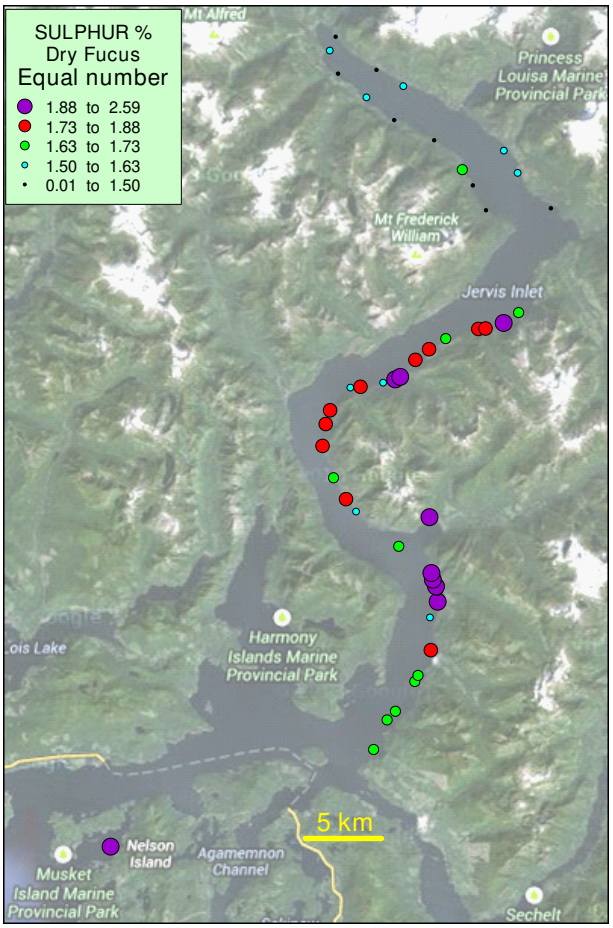
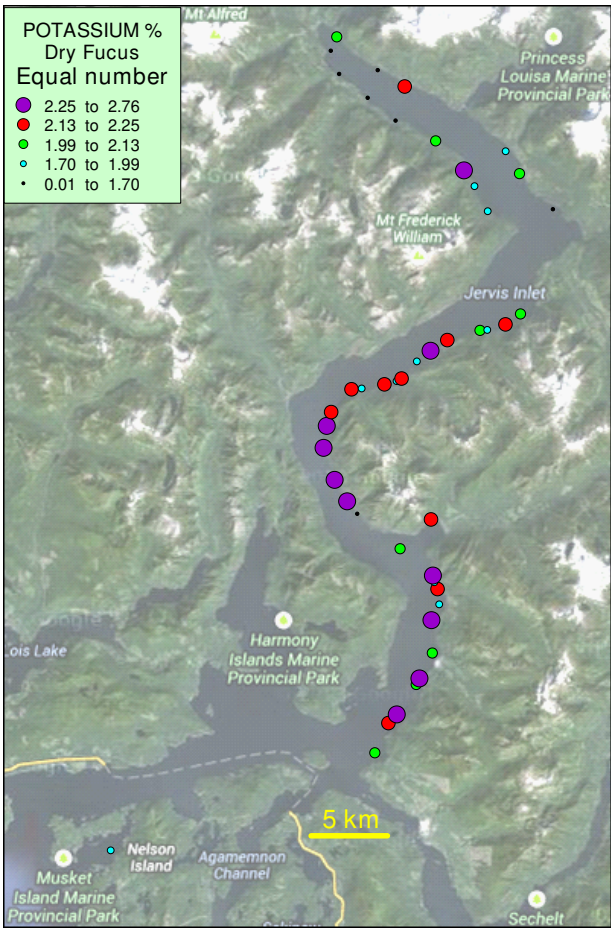


Figure 6: Re, Na, S and K oven-dried rockweed determined by ICP-MS.





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Forty-seven samples were collected from the shores of Jervis Inlet from which distinct zones of relative metal enrichments were identified:

1. Ag, As and several other commodity and pathfinder elements on the eastern shores toward the south end of the Inlet;
2. Cu, Mo, Ni, Co with associated Fe, REE and U at the northern end of the Inlet, suggesting a possible mineralized source upstream;
3. High enrichments of Re (with coincident Na, S and K) that are probably related just to the water salinity, since brown seaweeds are known to be biological sinks of Re in the sea;
4. Local enrichments of Au with coincident pathfinder elements.

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