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Seaweed as an Exploration Medium along the inlets of British Columbia – Part 2: Chemical variations and long-term changes - Howe Sound

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In a previous article we described the chemical variations of seaweed from the intertidal zone of Jervis Inlet, western Canada, focusing on the use of the brown rockweed known as wrack *(Fucus gardneri)* as a potential geochemical exploration medium that preserves the chemical variations of the surrounding coastal mountains (Dunn & McCaffrey 2017). A similar seaweed collection was made around Howe Sound from many of the same sites sampled 24 years earlier (Dunn *et al.* 1992), including the area down-drainage from the former Britannia Cu mine, 12 km south of Squamish (Fig. 1).

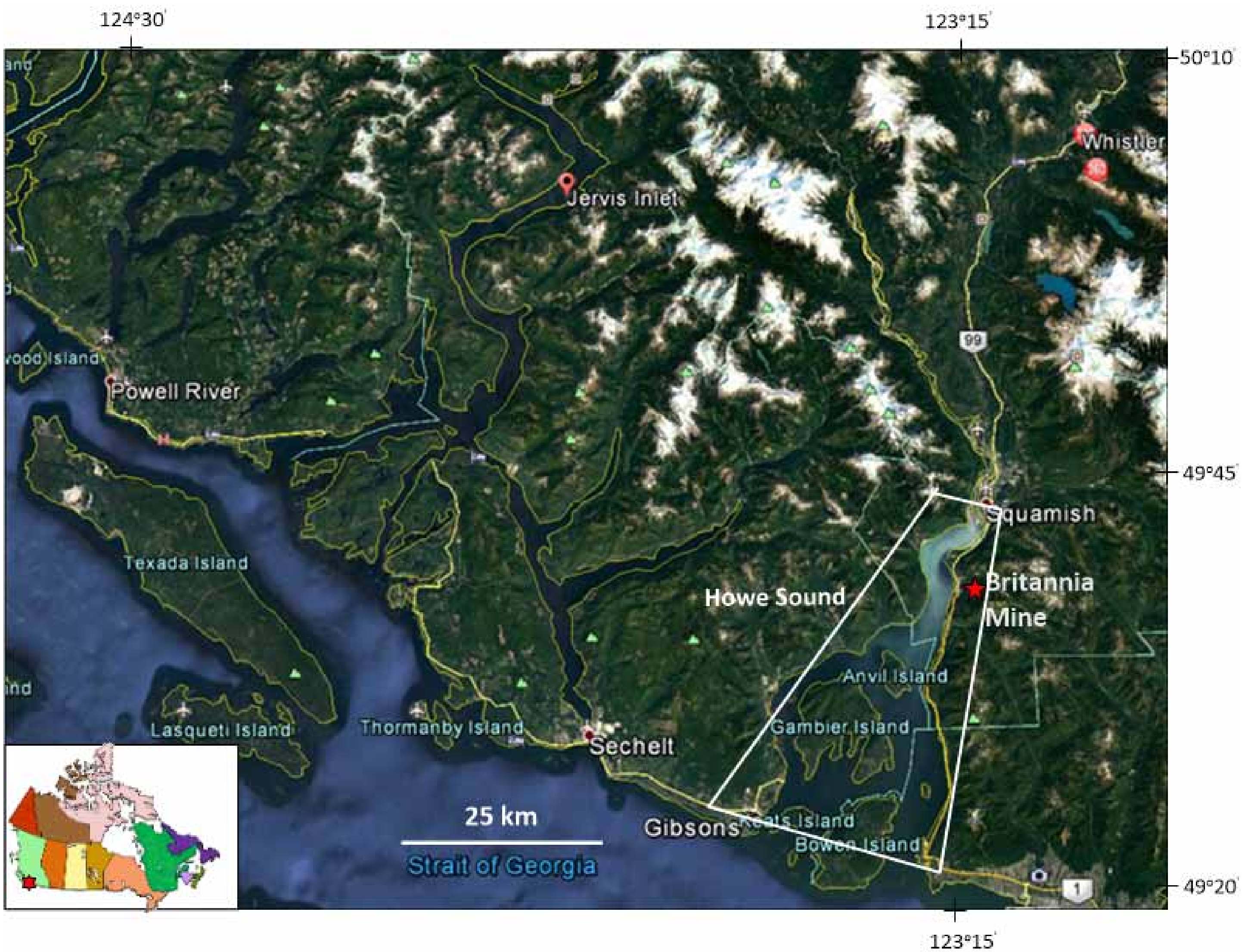

Figure 1. Location map, including Howe Sound, Jervis Inlet, and Britannia Beach on the west coast of Canada. *Map base is from Google Earth.*

Location

Horseshoe Bay, opposite Bowen Island, lies 15 km west of downtown Vancouver, at the southeastern end of Howe Sound. The Sound terminates at Squamish 40 km to the north where the Squamish River drains from the north, and is up to 40 km wide in the south and narrows to 3 km for the last 20 km. Of the several islands in the Sound, Bowen, Gambier, and Anvil are the largest. Highway 99 follows the eastern shore, passing through the small communities of Lions Bay and Britannia Beach (Fig. 1).

continued on page 5

Seaweed as an Exploration Medium…

continued from page 1

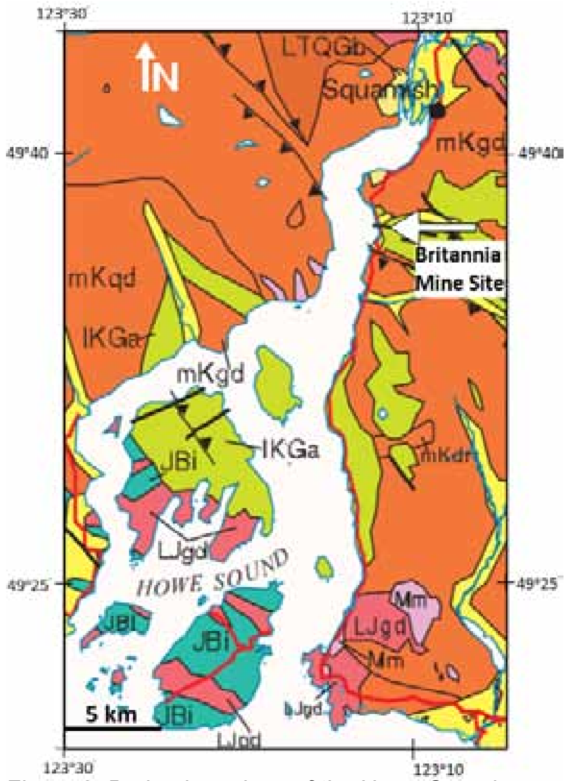

Figure 2. Bedrock geology of the Howe Sound area and location of the Britannia Mine. Yellow Quaternary sediments including LTQGb (Garibaldi Gp volcanic rocks); mKgd Middle Cretaceous granodiorite; mKqd Middle Cretaceous quartz diorite; IKGa Lower Cretaceous Gambier Gp, metavolcanics and metasediments; JBI Jurassic Bowen Island Gp, mostly metavolcanic rocks; LJad Late Jurassic andesite; LJGd Late Jurassic granodiorite; Mm Mississippian metamorphic rocks. Geology from http://www.empr.gov.bc.ca/Mining/Geoscience/PublicationsCatalogue/Maps/GeoscienceMaps/Documents/GM2005-03_South.pdf (after Armstrong 1990).

Environmental Setting and Geology

Howe Sound is located within the wet maritime forest (Coastal Western Hemlock Biogeoclimatic Zone) with steep mountains on either side. Water depth of the fjord averages 280 m south of a submarine ridge (14-61 m deep – "Porteau sill") north of Anvil Island located halfway up the Sound, and 240 m deep farther north. The bedrock geology of the sound area is shown in Figure 2.

In 1888, Cu was discovered in the mountains around Britannia Creek, 10 km south of Squamish, and in 1905 mining began. By 1929 it was the largest Cu mine in the British Empire. Mining continued until 1974, by which time it had produced 500,000 t Cu, 122,000 t Zn, 15,000 t Pb, 14,000,000 g Au, and 84,000,000 g Ag (Smitheringdale 2011). During the operations, a considerable amount of metal-rich sediment was discharged into Howe Sound and considerable efforts have gone into environmental remediation.

Seaweed (Rockweed *[Fucus]*) Survey

The seaweed survey was conducted in August of 2015 (applying the same sample collection and analytical procedures as those described in Part 1) collecting samples from 34 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 43 samples were submitted for analysis. The four splits of a rockweed

continued on page 6

Seaweed as an Exploration Medium… *continued from page 5*

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, Mo, Sb, Th, and Ge) that had concentrations close to the detection limits of the analytical method, yet yielded RSDs mostly better than 30%. The data for Mo exhibited poor accuracy so are omitted from this summary. The reproducibility of the field and laboratory duplicates varied from good to excellent for almost all elements. Analytical data are reported in Appendix A.

Results

Table 1 summarizes the element concentrations in the 34 samples and compares concentrations to the suite of 47 samples from Jervis Inlet, collected 2 years previously (Dunn & McCaffrey 2017). The highlighted median values show that Ag, Au, Ba, Ce, Co, Cu, La, Nd, Ti, and Y have concentrations more than 4 times higher in Howe Sound than Jervis Inlet; similar magnitudes of relative enrichment are shown for the maximum values.

HOWE (n=34)		D.L.	Median	Max.
Ag	ppb	2	100	128
As	ppm	0.1	27.65	44.8
Au	ppb	0.2	14.25	23.5
B	ppm	1	75	106
Ba	ppm	0.1	68.7	187.2
Ca	%	0.01	1.3	5.71
Cd	ppm	0.01	2.02	3.04
Ce	ppm	0.01	0.51	5.67
Co	ppm	0.01	3.385	6.11
Cr	ppm	0.1	3.65	32.4
Cs	ppm	0.005	0.056	0.268
Cu	ppm	0.01	7.895	88.16
Fe	%	0.001	0.032	0.476
K	%	0.01	2.905	3.92
La	ppm	0.01	0.405	3.11
Li	ppm	0.01	0.6	2.74
Mg	%	0.001	0.928	1.114
Mn	ppm	1	136.5	252
Na	%	0.001	2.6195	3.892
Nd	ppm	0.02	0.415	3.02
Ni	ppm	0.1	8.1	15.5
P	%	0.001	0.128	0.198
Pb	ppm	0.01	0.21	1.27
Rb	ppm	0.1	12.8	16.8
Re	ppb	1	18	47
S	%	0.01	3.395	3.77
Sb	ppm	0.02	0.115	0.35
Sc	ppm	0.1	0.2	1
Se	ppm	0.1	0.5	1
Sm	ppm	0.02	0.06	0.63
Sr	ppm	0.5	711.2	934.8
Ti	ppm	1	12.5	283
U	ppm	0.01	1.12	4.08
Y	ppm	0.001	0.45	2.931
Zn	ppm	0.1	34	214
Zr	ppm	0.01	0.21	1.07

Mo omitted - v. poor accuracy at Howe Sound

JERVIS (n=47)	Median	Max.
Ag	23	63
As	15.7	26.5
Au	0.7	4.6*
B	86	121
Ba	12.6	30.4
Ca	1.32	2.59
Cd	1.7	3.02
Ce	0.07	1.24
Co	0.56	3.19
Cr	2.1	18.1
Cs	0.037	0.149
Cu	1.54	5.58
Fe	0.014	0.37
K	2.04	2.76
La	0.06	0.6
Li	0.28	2.36
Mg	0.66	0.88
Mn	35	122
Na	1.455	2.82
Nd	0.06	0.65
Ni	3.6	11.6
P	0.083	0.138
Pb	0.07	0.67
Rb	8.9	10.7
Re	18	43
S	1.67	2.59
Sb	0.12	0.24
Sc	0.2	0.6
Se	0.3	0.5
Sm	<0.02	0.14
Sr	521	886
Ti	2	158
U	0.9	1.66
Y	0.102	0.749
Zn	16.5	46.5
Zr	0.10	0.24

*Less 1 high Au value that was not reproduced by resampling in 2017

Median Howe:Jervis	Maximum Howe:Jervis
4.35	2.03
1.76	1.69
20.36	5.11
0.87	0.88
5.45	6.16
0.98	2.20
1.19	1.01
7.29	4.57
6.04	1.92
1.74	1.79
1.51	1.80
5.13	15.80
2.29	1.29
1.42	1.42
6.75	5.18
2.14	1.16
1.40	1.26
3.90	2.07
1.80	1.38
6.92	4.65
2.25	1.34
1.54	1.43
3.00	1.90
1.44	1.57
1.00	1.09
2.03	1.46
0.96	1.46
1.00	1.67
1.67	2.00
	4.50
1.37	1.06
6.25	1.79
1.24	2.46
4.41	3.91
2.06	4.60
2.10	4.46

Table 1. Element concentrations in dry rockweed – Comparison of Howe Sound with Jervis Inlet.

continued on page 8

Seaweed as an Exploration Medium… *continued from page 6*

Figure 3 shows the relatively high levels of Cu and Zn in samples from close to Britannia Beach. Lead values are elevated, but quite low, whereas Ag values show a stronger dispersion toward the southwest. The pattern for Ag has closer similarities to Au than base metals, perhaps indicating relative Au enrichment from a source on the west side of the Sound

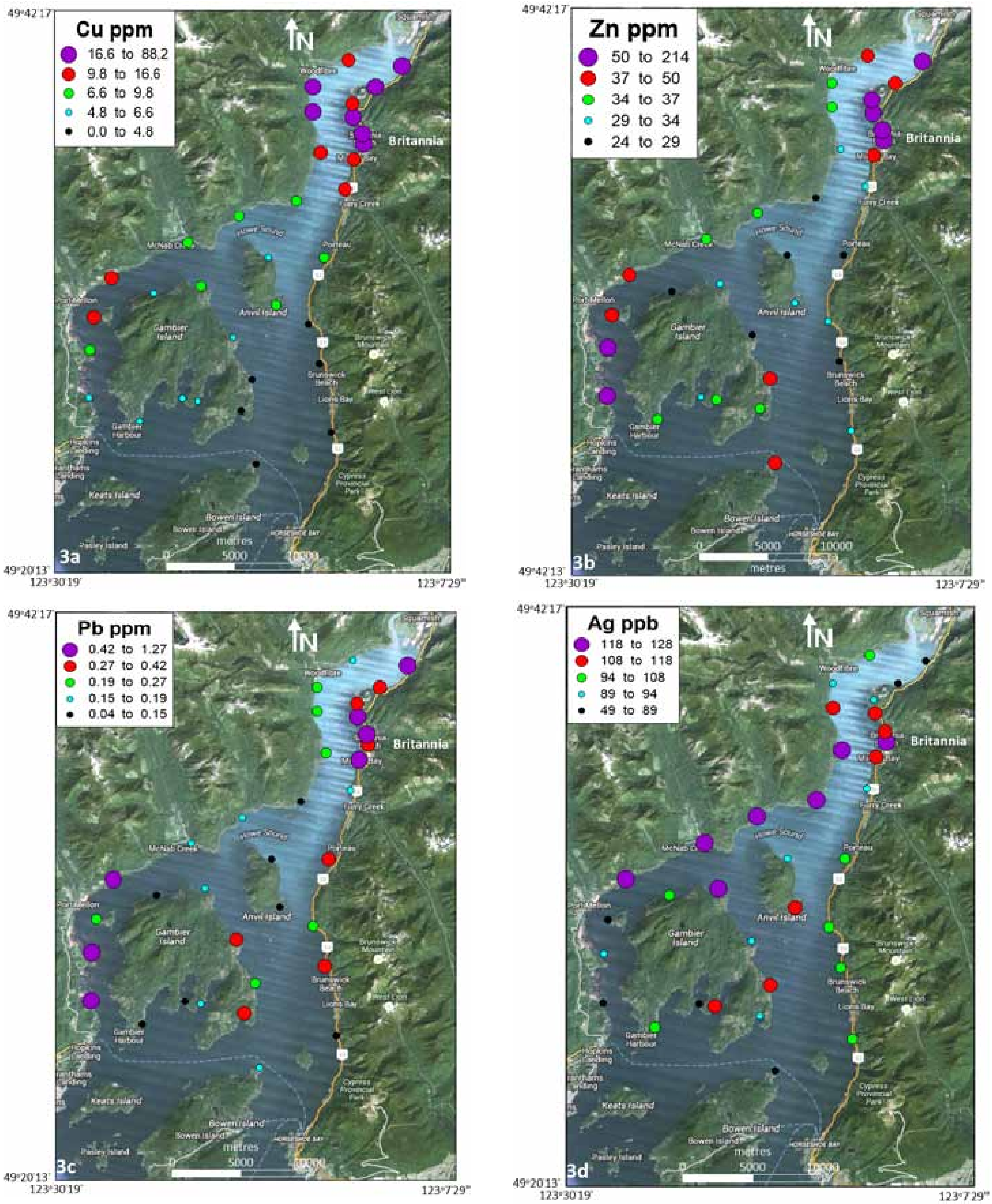

Figure 3. Cu, Zn, Pb, and Ag concentrations in dry rockweed determined by modified aqua regia/ICP-MS.

continued on page 9

Seaweed as an Exploration Medium… *continued from page 8*

(Fig. 4) – e.g. McNab Creek (north of Gambier Island). Arsenic exhibits a similar pattern to Au, but shows more dispersion down the eastern channel.

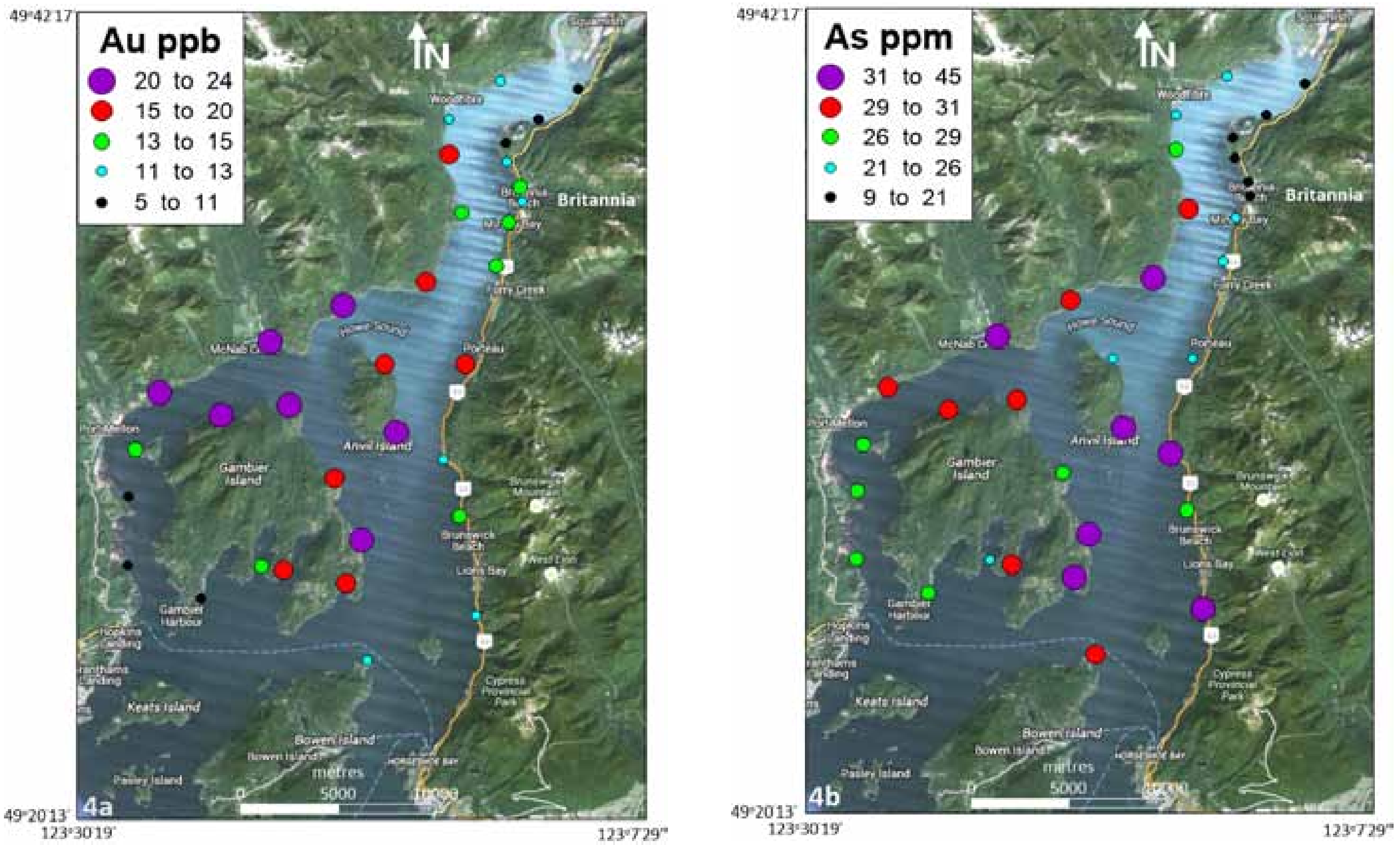

Figure 4. Au and As concentrations in dry rockweed determined by modified aqua regia/ICP-MS.

continued on page 10

Seaweed as an Exploration Medium… *continued from page 9*

At the north end of the Sound, where there is an abundance of water and sediment draining from the Squamish River, there are relatively high concentrations of Co and Cr (Fig. 5) with associated Ba, Fe, Ni, REE, Hg, and U (not shown) indicating a possible mineralized source upstream. However, a similar suite of elements was noted in the upper reaches of Jervis Inlet (Dunn & McCaffrey 2017) suggesting that this might be related to a higher influx of fresh water compared to farther south.

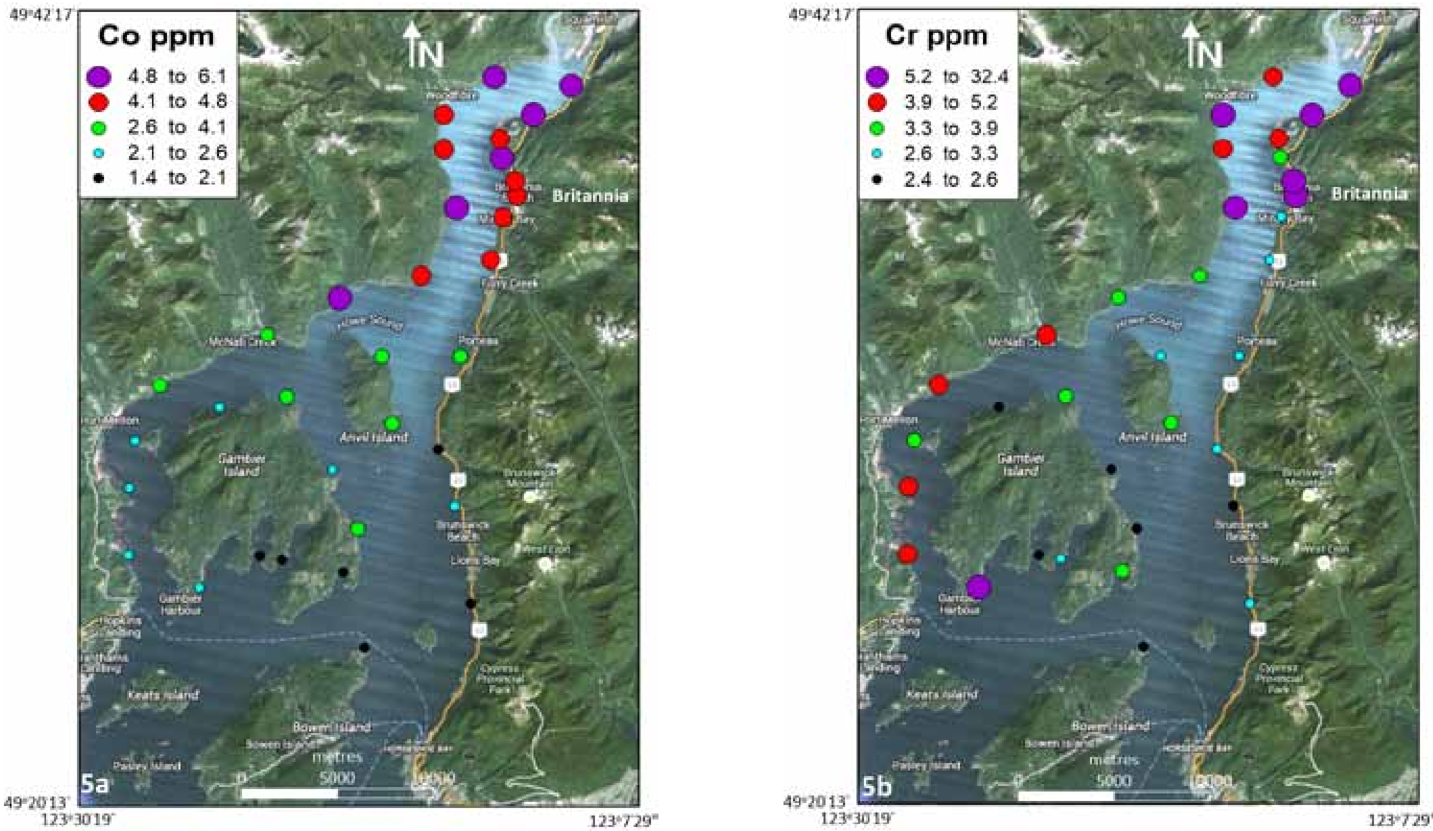

Figure 5. Co and Cr concentrations in dry rockweed determined by modified aqua regia/ICP-MS.

Rhenium concentrations in vegetation are typically <1 ppb re, but in brown seaweed the saline environment results in much higher levels. The highest concentrations of Re are mostly at the southern end of Howe Sound and, as at Jervis Inlet, it is surmised that the low concentrations in the north may be because that area has a higher concentration of fresh water from stream meltwaters draining from the mountains, resulting 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 (Fig. 6). This may be a consistent pattern in the coastal fjords.

continued on page 11

Seaweed as an Exploration Medium… *continued from page 10*

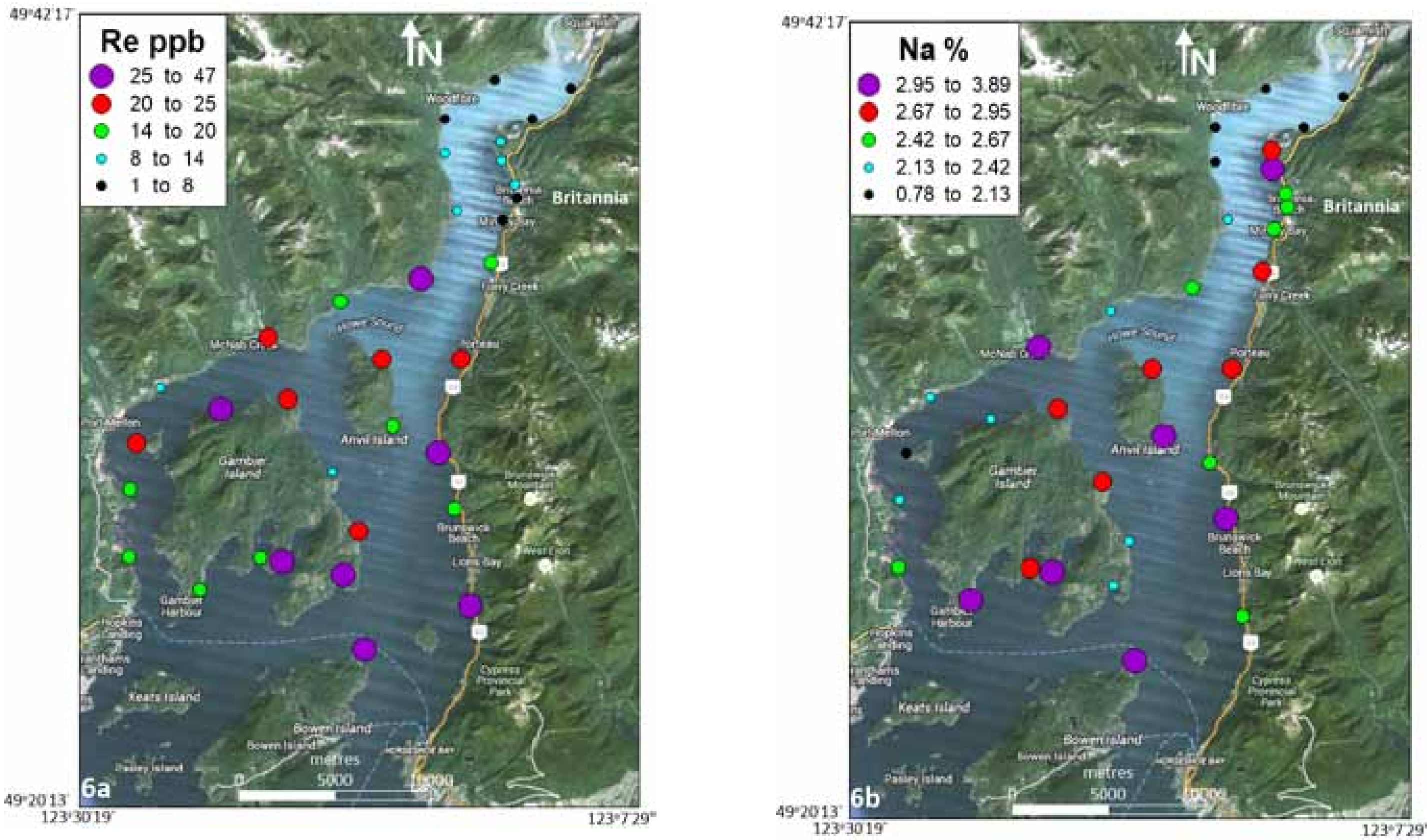

Figure 6. Re and Na concentrations in dry rockweed determined by modified aqua regia/ICP-MS.

Long-term changes in seaweed chemistry

Figure 7a shows the Britannia Mine Museum. The mine site was to the left of the museum, and drainage down the valley carried metal rich sediments for many years, with the result that shoreline rocks on either side of the stream became heavily stained and no seaweed grew for a distance of 1.5 km to both the north and south of Britannia Beach (Dunn et al. 1992) – Fig. 7b.

Where the seaweed first appeared in 1991, it was stunted and contained 540 ppm Cu and 300 ppm Zn (Table 2).

Year	Copper (ppm) Median	Copper (ppm) Max	Zinc (ppm) Median	Zinc (ppm) Max
1991	120	540	160	300
2015	7	88	35	210

Table 2. Long term changes in concentrations of Cu and Zn in dry rockweed – same location resampled in 2015.

Although the rock staining persists to today, the seaweed now grows in the previously barren zone and concentrations of both Cu and Zn are substantially lower in samples collected near the former mine site in 2015, presumably because of the extensive environmental remediation that had taken place over the previous quarter century. Cadmium (~2 ppm) and Hg (~10 ppb) had similar low concentrations in 1991 and 2015.

continued on page 12

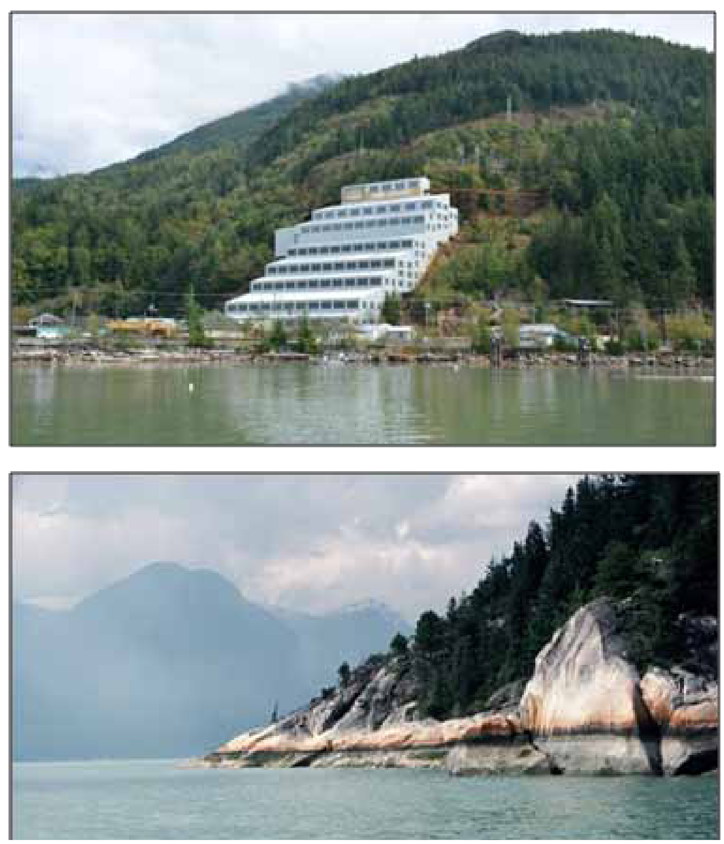

Figure 7. a) Britannia Mine Museum, drainage is down the valley to the left of the mine building; b) 1 km north of Britannia in 1991 - high-tide staining of rocks from effluents in Britannia Creek that drained into Howe Sound.

Seaweed as an Exploration Medium… *continued from page 11*

Summary and Conclusions

The brown rockweed *Fucus* grows in abundance in the intertidal zones of the western shores of Canada and the USA, and is easy to collect by boat. Where a stream cuts through mineralization, the waters can become enriched in elements associated with the mineralization. Many streams drain into the abundant sounds along the northwest coast of the USA and Canada where their elevated metal signatures can be readily reflected in the rockweed close by. Therefore, if seaweed is relatively enriched in a commodity metal (and/or its pathfinder elements) a focus is provided for more detailed follow up into the mountains to seek the source.

Thirty-four samples were collected from the shores of Howe Sound. Distinct zones of relative metal enrichments were identified:

1. Notably Cu and Zn close to Britannia Beach, and undoubtedly derived from the former Britannia mine;
2. Pb and Ag also moderately enriched near Britannia Beach, but with Ag exhibiting similar enrichments along the western shore, opposite Gambier Island;
3. Highest Au levels were at similar sites to the highest Ag, suggesting an area of slight precious metal enrichment north of Gambier Island and possibly introduced into Howe Sound from McNab Creek. Arsenic dispersion, commonly associated with Au, extends from this area to the southeast;
4. Co and Cr present a different picture with highest levels (associated with Ba, Fe, Ni, REE, Hg, and U) in the north, suggesting drainage from a mixed source dominated by mafic rocks north of Squamish;
5. High enrichments of Re and Na are probably related to water salinity, since brown seaweeds are known to be biological sinks of Re in the sea (Yang, 1991);
6. Samples collected in 1991 from sites near Britannia Beach were resampled in 2015 and found to contain significantly lower concentrations of Cu and Zn than previously, attesting to the efficiency of the steady clean-up efforts over the past quarter century.

It is concluded that the rockweed *Fucus* can be a useful sample medium for providing focus to exploring for sources of metal enrichments, and can be used for long-term environmental monitoring.

Acknowledgements

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