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Selected Metal Levels of Commercially Valuable Seaweeds Adjacent to and Distant from Point Sources of Contamination in Nova Scotia and New Brunswick

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The harvesting of marine plants on a commercial scale was a significant industry in the Maritime Provinces of Canada by the end of World War II.Total landings reached 40,000 tonnes wet weight with a value $5.5 million in 1974. The harvest consists primarily of Chondrus crispus Stackhouse ("Irish moss") and Ascophyllum nodosum (Linnaeus)LeJolis ("rockweed"). Other species of minor or potential commercial importance are Furcellaria fastigiata (Hudson), Lamouroux ("wireweed"), Palmaria palmata Guiry ("dulse"), Gigartina stellata (Stackhouse), Batters ("Fundy moss"), Laminaria digitata (Linnaeus), Lamouroux ("horsetail kelp"), and Laminaria longicruris De la Pylaie ("broadleaf kelp"). These seaweeds have been traditionally utilized as foodstuffs either as a processed extract or a semi-processed plant.

The Maritime coastline is becoming industrialized; there is also potential for expansion of the marine plant industry beyond traditional harvest areas. Therefore, the quality of material from new areas must be examined prior to exploitation as well as monitoring of traditional areas.

The bioaccumulation of metals by marine plants was recognized in early measurements of trace element concentrations which were factorially above ambient water values (Black 1952). It was due to this property that Laminaria species were harvested early in this century for their iodine content. However, in areas where significant industrial sources of heavy metal pollution occur, excessively high concentrations of metals accumulate in plant tissue (Bryan and Hummerstone 1973). Very high ambient concentrations of heavy metals can lead indirectly to a decline in algal diversity and productivity (Rueness 1973). This is particularly true for early life stages such as young Laminaria sporophytes (Hopkin and Kain 1978).

Before growth and reproductive inhibition are caused by severe effects of heavy metal pollution, food quality changes may occur. The Canadian Food and Drug Act (Dept. of National Health and Welfare Canada 1984) does not specifically schedule heavy metals for seaweeds; it does give maximum levels for other foodstuffs. The Food Chemical Code (U.S.A.) (National Research Council 1972) limits heavy metals in the extracts of seaweeds. Sediment and water samples taken in connection with the Ocean Dumping Control Act of Canada have identified several sites with elevated heavy metal content in the Maritimes (Environment Canada, unpublished data).

The purpose of this study was to examine heavy metal levels in commercially important seaweeds from traditional harvest areas and areas near point sources of pollution. We wished to provide a baseline for the future and identify existing problem areas.

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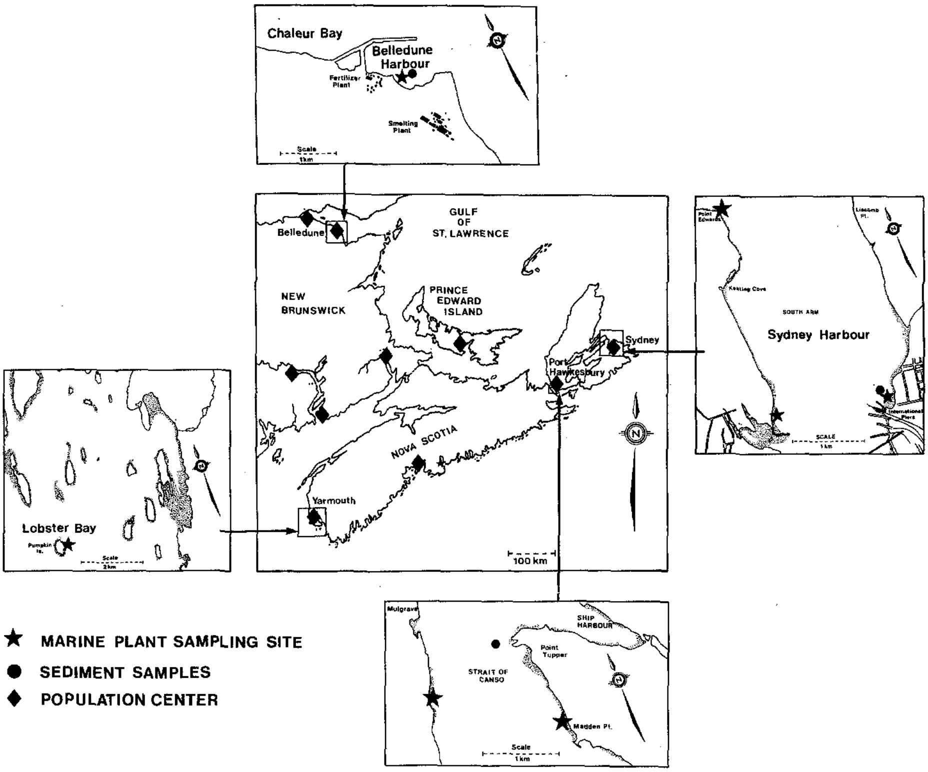

Figure 1. The Atlantic provinces of Canada, inserts: location of marine plant sampling stations for selected metal analysis.

MATERIALS AND METHODS

Species collected were Chondrus crispus, a red algae harvested for the phycocolloid carrageenan; Ascophyllum nodosum, a brown algae producing the phycocolloid alginate; Laminaria longicruris ; and Laminaria digitata, potentially harvestable for animal fodder,human specialty food, and alginate. Not all species were available at every site; Fucus sp. was substituted for A. nodosum when necessary.

Four sampling areas (Fig. 1) selected for the study were as follows:

1) Pumpkin Island, Lobster Bay, Yarmouth County, N.S. - an actively harvested marine plant bed. This area has a very large (4 m) tidal amplitude, providing a rapid exchange of water. In 1983, there were no point sources of heavy metal contamination in Lobster Bay.

2) Sydney Harbour, Cape Breton, N.S. - a series of three stations were sampled successively further away from a point source of pollution, the Sydney Steel Plant (Fig. 1); a station at the mouth of Sydney Harbour, Point Edwards, was near coal washing and waste sites.

3) Madden Point and Mulgrave, in Chedabucto Bay,N.S. are in a formerly active industrial area of refineries and a superport.

4) Belledune Harbour, N.B. - two stations were sampled near the site of a lead smelter with a history of chronic heavy metal contamination (Uthe and Zitko 1980).

Marine sediments near all sites except Pumpkin Island, Lobster Bay, N.S.have elevated levels of one or more heavy metals in contrast with deep-water sediments remote from point sources of contamination (Table 1). Belledune Harbour was unique, with very high cadmium (Cd) levels compared to all other sites.

Collections from these sites were completed in two series, June and August 1983.Due to the complex morphology and size of these macrophytes, it was necessary to dissect whole plants into segments based on age for A. nodosum (1 to 6 yr), size in C. crispus (less than 6 cm, more than 6 cm), and plant structure in Laminaria spp. (stipe, blade). These segments (a minimum of 100 g dry weight) from 10 to 30 fronds were placed in coolers and returned to the laboratory within 24 h. These were washed with deionized-distilled water, dried at 80°C for 24 h, and ground in non-metallic vessels. Water samples, 500 mL, were taken at each site for trace metal analysis at 10-cm depth.

Table 1. Marine sediment concentrations of selected heavy metals (mg kg^{-1}) near point sources in Maritime Canada.

Location	Cd	Cu	Pb	Zn
Port Hawkesbury Point Tupper	0.45-0.64	37.0-40.0	45.0- 50.0	116-125
Sydney (International Piers)	0.1- 1.3	12.0-55.7	27.5-197.0	99-494
Belledune Harbour	5.4	42.8	229.0	510
Entrance to Chedabucto Bay (180 m depth)	0.1	23-30	28-34	75- 80

A dried plant sample (0.5 g) was treated with concentrated HNO_3(10 mL)for 24 h at room temperature. The mixture was then heated to near dryness. The residue was ashed at 450°C for 2 h in a muffle furnace. The ash was digested with concentrated HNO_3 (10mL).After drying,the residue was dissolved in 5mL HNO_3 (25% v/v) and made to 100mL volume.The concentration of chromium (Cr), copper (Cu), iron (Fe), lead (Pb), zinc (Zn), and nickel (Ni) were determined using an Inductively-Coupled Argon Plasma atomic emission spectrometric method (Jarrel Ash Plasma Atom Comp 975). Cd was analysed by the flameless atomic absorption spectrometric method as recommended by the manufacturer (Perkin Elmer 403 and HGA 2100). The metals in sea water were determined by chelation with ammonium pyrrolidine dithiocarbamate and extraction into methyl isobutyl ketone and aspirating organic extract directly into the flame (American Public Health Association et al 1980). National Bureau of Standards Standard Reference Material 1571 Orchard Leaves analyzed for the measured metals showed agreement within the range of 90 to 107% of the certified values.

RESULTS AND DISCUSSION

Values for metal content of seaweed tissue from all sites except Belledune Harbour were combined to examine variation in metal content between plant structures for each species. There were no significant differences in metal concentrations which could be correlated with age, size, or plant structure ($P=<0.05$). Some trends toward differences between plant structures were found at the Belledune Harbour site; however, sample size was too small to define significance at this site. Therefore, all values for separate portions of each algal species were combined in subsequent comparisons.

C. crispus sampled near the most chronic sources of heavy metal pollution, Belledune Harbour, had significantly higher ($P<0.05$) Pb values than other species collected at the same site (Table 2). A. nodosum reached the highest mean levels of Cd and Zn at the Belledune Harbour site, 15 times the mean Pumpkin Island values for this species. In contrast, Fe occurred at high concentration (>1,000 mg kg^{-1}) in all three species at Sydney Station 2. Cu concentrations were lowest in Laminaria spp. tissues by a factor of two compared to other species at four of the seven stations (Table 2). At the control site, A. nodosum and C. crispus had higher levels of Fe and Zn than Laminaria spp. (Table 2). Dry weight composition accounted for some of these differences between species A. nodosum (0.25 dry matter content), C. crispus (0.19), and Laminaria (0.14 to 0.16).

Cd levels in Belledune Harbour plant tissues were 2 to 22 times values found at other sites (Table 2). Maximum values reached 10.2 mg kg^{-1} in 10-yr-old segments of A. nodosum. Pb values of C. crispus from this area were seven times control area levels. Zn peaked in 10-yr-old A. nodosum segments ten times mean values for the control area (Table 2). Highest Fe levels were found adjacent to the Sydney Steel plant (Station 2), 10 times the Pumpkin Island value for C. crispus and 156 times L. longicruris values. Point Edwards and, Sydney Harbour Station 1 , had two to four times Fe levels of "the control" site (Table 2). There were no significant differences ($P<0.05$) in concentrations of the metals in the samples collected from the non-industrialized southwestern Nova Scotia site and the industrialized area of the Canso Strait (Madden Pt.,Mulgrave) (Table 2). There were occasional high values for Pb but no overall indications of chronic heavy metal contamination.

Ambient water samples from all sites were at or below 1 $\mu g\ L^{-1}$ for Cd and Cu; Pb and Zn ranged between 0.1 $\mu g\ L^{-1}$ and 6 $\mu g\ L^{-1}$ at all sites except Sydney Station International Piers where 11 $\mu g\ L^{-1}$ was obtained in one sample.

Those locations identified as contaminated by high tissue concentrations of metals (Belledune Harbour, Sydney Harbour) are not areas which have active commercial harvesting of marine plants. Although the Canadian Food and Drug Act does not address the heavy metal content of seaweeds, guidelines for other food materials indicate lead values of 10 mg kg^{-1} of dry matter are of concern. Phycocolloid extracts are restricted in the Food Chemicals Code (U.S.A.) to a maximum of 10 mg kg^{-1} Pb in carrageenan, which is a 40-60% component of C. crispus.

In a global context the highest levels reported for Pb and Zn in seaweeds were by Melhuus et al. (1978) for a Norwegian site, five to ten times levels found in our study (Table 3). However, Cd levels in seaweeds from Belledune Harbour are among the highest recorded, and Pb values were similar to those found in contaminated British estuaries (Bryan and Hummerstone 1973).

Very few seaweed tissue values for Fe are reported in the literature, but maximum values found for fucoid species in our study are relatively high. However, the majority of the sites sampled have Fe values well below the metal levels reported from Europe, including the early study of Black and Mitchell (1952). There were some metals analyzed from samples in southwestern Nova Scotia in the study of Young and Langille (1958) (Table 3). Cu values were ten times higher in the earlier study in C. crispus; however, Zn and Cu are similar for A. nodosum. Analytical methods have

Table 2. Tissue concentrations (n=3-5)* of selected metals from commercial seaweeds in Maritime Canada (mg kg^{-1} ± sd dry weight).

Species	Location	Cd	Cr	Cu	Fe	Pb	Zn	Ni
Ascophyllum nodosum	Belledune	9.0±2.3	1.9±1.6	5.3±1.7	104±50	9.9± 1.8	350±70	1.0±0.2
Chondrus crispus		2.4±2.2	1.5±0.6	5.7±1.6	390±41	33.1± 0.6	76±10	3.1±0.4
Laminaria longicruris		2.1±0.4	1.2±0.3	1.7±0.4	86±60	8.5± 1.4	56±23	1.5±0.6
Fucus sp	Sydney Stn. 1	0.6±0.4	1.5±0.8	4.5±2.5	620±495	2.3± 0.5	46±19	2.9±2.0
Chondrus crispus		0.4±0.1	1.7±0.4	5.8± 0.6	430±470	6.1±1.6	3.8± 2.8	5.3±0.2
Laminaria longicruris		0.5±0.3	1.0*	1.6±0.2	270±150	2.1± 0.2	26±10	1.0±0.1
Fucus sp.	Sydney Stn. 2 (steel plant wharf)	1.2±0.2	2.7±0.8	7.3±1.3	1,500±230	3.9± 1.0	70± 5	6.0±2.3
Chondrus crispus		0.5±0.2	2.6±0.2	9.1±4.6	1,100±200	8.3± 1.5	53±14	12.8±4.2
Laminaria longicruris		0.9±0.6	2.0±1.0	2.5±0.3	8,700±760	2.3± 0.3	25±11	1.5±0.5
Ascophyllum nodosum	Point Edwards	0.5±0.1	1.0*	3.1±0.4	370±190	2.0*	27±14	1.2±0.3
Fucus sp.		0.6±0.2	1.0*	1.8±0.8	130± 50	2.0*	21± 8	1.6±0.3
Chondrus crispus		0.4*	1.4*	3.9*	350±250	3.0± 1.3	26±1	6.8*
Laminaria digitata		0.2±0.1	4.85±5.4	1.5±0.6	10± 96	3.4± 0.8	29±10	1.0*
Laminaria longicruris		0.5±0.3	2.3±2.2	1.0*	90± 50	2.0*	22±6	1.0*
Chondrus crispus	Madden Pt.	0.3*	3.1±0.1	2.3±0.2	60± 2	3.1± 0.9	28±15	2.5±1.0
Fucus sp.		1.0±0.3	2.5±0.3	3.4±0.1	84± 24	14.6±18.0	30±6	4.7±4.1
Laminaria longicruris		0.5±0.3	2.7±0.4	2.1±0.8	41± 5	5.5± 3.4	35±19	1.3±0.4
Chondrus crispus	Mulgrave	0.4±0.1	3.2±2.1	4.8±1.9	7.6±4.4	7.6± 4.4	35±9	8.2±3.6
Fucus sp.		1.4±0.2	1.7± 0.9	5.8±1.6	100± 14	4.6± 3.3	25±8	3.1±2.1
Laminaria longicruris		1.2±1.2	3.0±0.7	5.8±2.9	370±420	57.6±70.4	25±15	4.5±2.7
Ascophyllum nodosum	Pumpkin Island (control site)	0.6±0.2	1.8±1.1	2.2±1.3	160±200	7.6± 5.8	32± 3	1.0±0.1
Chondrus crispus		0.5±0.1	1.3±0.1	2.6±0.4	120± 45	4.6±0.9	48±3	7.9±0.3
Laminaria digitata		0.4±0.1	1.3±0.4	2.9±1.0	47± 37	7.1± 4.9	20±6	1.0±0.1
Laminaria longicruris		0.8±0.5	1.4±0.3	2.8±0.6	56±33	10.7±5.2	18± 3	1.6±0.8

*Where no sd is shown, only single values were available.

improved substantially since 1952, and this may in part explain the differences between these studies.

The longevity of the species sampled is reflected by the relative accumulation of some metal concentrations. A. nodosum can live for 12 yr or more, C. crispus fronds for 2 to 3 yr, and Laminaria spp from 1.5 to 2 yr. Since the mechanism for uptake varies from metal to metal, a simple direct correlation was not expected. However, Zn, which is irreversibly accumulated, would show a chronological series in species subjected to identical ambient levels with time (Skipnes et al. 1975). In areas where there is not a chronic heavy metal problem it is probable a large number of samples would be required to register the differences between metal concentrations in tissues of various ages. At Belledune Harbour A. nodosum fronds (apical tips) and stems (stipes) averaged 5.5 mg kg^{-1}Cd and 6.2 mg kg^{-1} Cd respectively in an earlier study (Ray et al. 1980).

Table 3. Concentration of selected metals (mg kg^{-1}) in northern Atlantic seaweeds from selected studies.

Study	Algae	Fe	Mn	Zn	Ni	Cu	Pb	Cd
Preston et al (1972)	Fucus vesiculosus	111	96	489	3.66	8.3	7.2	1.70
Bryan and Hummerstone (1973)	Fucus vesiculosus	728	128	1,240		301	10	
Ray et al. (1980)	Fucus vesiculosus							1.3-30.3
	Ascophyllum nodosum							0.3-18.0
	Laminaria digitata							0.4- 1.8
Sirota and Uthe (1979)	Palmaria palmata			81.5		6.33	3.50	1.49
Bohn (1979)	Fucus distichus	345		138		3.3		1.2
Melhuus et al. (1978)	Fucus vesiculosus			2,207			135.8	9.3
	Ascophyllum nodosum			3,700		114.5	85.0	15.0
Black and Mitchell (1952)	Ascophyllum nodosum		116		3.7	12	4	
	Laminaria digitata		59		1.8	6	7	
Young and Langille (1958)	Chondrus crispus		64			20		
	Ascophyllum nodosum		35			6		

It is interesting to note that high levels of Cd, Zn, and Pb were not found in water samples of Belledune Harbour. Waste treatment was introduced at the smelting plant in 1980, reducing Cd contamination (Uthe et al. 1986). The high levels of metals in young plant tissues may be due to adsorption processes from old contaminated sediments or from periodic spills.

In conclusion, heavy metal contamination must be extreme and chronic to cause significant problems with quality and productivity of our marine plant resources. The locations of our traditional and potential harvesting areas are remote from any such point sources

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