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ORIGINAL ARTICLE

Kelp as a Bioindicator: Does it Matter Which Part of 5 M Long Plant is Used for Metal Analysis?

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Abstract Kelp may be useful as a bioindicator because they are primary producers that are eaten by higher trophic level organisms, including people and livestock. Often when kelp or other algae species are used as bioindicators, the whole organism is homogenized. However, some kelp can be over 25 m long from their holdfast to the tip of the blade, making it important to understand how contaminant levels vary throughout the plant. We compared the levels of arsenic, cadmium, chromium, lead, manganese, mercury and selenium in five different parts of the kelp *Alaria nana* to examine the variability of metal distribution. To be useful as a bioindicator, it is critical to know whether levels are constant throughout the kelp, or which part is the highest accumulator. Kelp were collected on Adak Island in the Aleutian Chain of Alaska from the Adak Harbor and Clam Cove, which opens onto the Bering Sea. In addition to determining if the levels differ in different parts of the kelp, we wanted to determine whether there were locational or size-related differences. Regression models indicated that between 14% and 43% of the variation in the levels of arsenic, cadmium, chromium, manganese, mercury, and selenium was explained by total length, part of the plant, and location (but not for lead). The main contributors to variability were length (for arsenic and selenium), location (mercury), and part of the plant (for arsenic, cadmium, chromium and manganese). The higher levels of selenium occurred at Clam Cove, while mercury was higher at the harbor. Where there was a significant difference among parts, the holdfast had the highest levels, although the differences were not great. These data indicate that consistency should be applied in selecting the part of kelp (and the length) to be used as a bioindicator. While any part of *Alaria* could be collected for some metals, for arsenic, cadmium, chromium, and manganese a conversion should be made among parts. In the Aleutians the holdfast can be perennial while the blade, whipped to pieces by winter wave action, is regrown each year. Thus the holdfast may be used for longer-term exposure for arsenic, cadmium, chromium and manganese, while

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the blade can be used for short-term exposure for all metals. Cadmium, lead and selenium were at levels that suggest that predators, including people, may be at risk from consuming *Alaria*. More attention should be devoted to heavy metal levels in kelp and other algae from Adak, particularly where they may play a role in a subsistence diets.

Keywords *Alaria* · Algae · Aleutian Islands · Bioindicator · Cadmium · Kelp · Lead · Mercury

1 Introduction

Governmental agencies, non-governmental organizations, Tribal Nations, scientists, conservationists, managers, regulators, and the public are increasingly interested in assessing the health of species, populations, communities and ecosystems. Biomonitoring to establish baseline conditions of contaminant exposure is an important part of environmental assessment. Since ecosystems have tens, hundreds, or thousands of individual species, it is impossible to assess the health of all organisms. Instead, it is essential to develop a suite of bioindicators that can be used to assess status and trends within that ecosystem (Piotrowski 1985; Peakall 1992; Burger and Gochfeld 2001, 2004a; Carignan and Villard 2001; Burger 2006). Bioindicators and biomarkers need to be developed to fit the specific assessment needs of the ecological community or ecosystem, within the framework of governmental, Tribal or public needs.

Developing bioindicators for marine ecosystems provides unique challenges because of the tidal regime, vertical stratification of organisms, and the difficulty of collecting benthic organisms. Marine ecosystems in remote areas provide additional challenges because of the difficulties of deploying divers far from compression chambers and other emergency medical facilities. Under such circumstances, it is advantageous to develop bioindicators for the sublittoral or benthic zone that can be collected without the use of divers. Macroalgae provide this opportunity, because many species are attached to the bottom, but have blades that extend to the surface. The tops of macroalgae blades could be collected from small boats at different distances from the shore.

In this paper we examine the use of kelp as a bioindicator to assess the risk to human and ecological health, and to monitor contaminated sites. Kelp are used as a food and for medicinal purposes in many places in the world, making them useful as a bioindicator. Specifically, we examine the levels of arsenic, cadmium, chromium, lead, manganese, mercury and selenium in five sections of the kelp *Alaria nana*, collected from Adak Island, Alaska, located in the Aleutians, in 2004. We were particularly interested in whether the levels varied between the holdfast and the upper tip of the blade, the section most easily collected without the use of divers. Most papers dealing with kelp and other algae do not identify the part of the plant that was sampled, or whether it was taken consistently from the same place on the plant. Developing bioindicators for the marine environment of the Aleutians is particularly valuable because of past military activity on many of these islands, and the use of Amchitka Island as a site of underground nuclear testing from 1965–1971 (Kohlhoff 2002; Younker 2002). We were also interested in whether there were locational differences (between Clam Cove and Adak harbor) or size differences (did metal levels change with length of the algae).

Marine and estuarine macroalgae concentrate some metals to levels many times higher than levels found in surrounding waters, due partly to passive and active accumulation, and to the metal sequestration in vacuoles rich in polyphenols (Ragan et al. 1979). Metals may be adsorbed onto the surface of the plant. Algae have been used in phytoremediation, where the algal biomass is removed to reduce aquatic contaminant loads (Caliceti et al. 2002; Mehta and Gaur 2005). Macroalgae apparently take up some metals in proportion to the external concentration in surrounding water (Phillips 1990). For some algae, metal concentrations vary in different portions of the plant; levels are higher in older parts of the algae (Black and Mitchell 1952; Bryan 1969, 1971; Bryan and Hummerstone 1973; Fuge and James 1973, 1974; Young 1975; Phillips 1990). Sanchiz et al. (1999) found no differences in different parts of the algae *Calerpa prolifera* from Spain.

Kelp are important components of marine ecosystems in the Aleutians, and are part of the sea urchin (*Strongylocentrotus polyacanthus*)–sea otter (*Enhydra lutris*) food chain. When sea otters disappear, sea urchins increase because of lack of predation, and there is reduced growth of the kelp beds (CAFF 2001). Both the presence of sea urchins, and of full grown kelp prevent recruitment of new kelp into an area (Dean et al. 1989). In the Aleutians, the sublittoral floating kelp beds, mainly of *Alaria* spp. and *Cymathere* spp., are dense enough to impede small boat traffic (Powers et al. 1960). Some species of *Alaria* have blade lengths in excess of 25 m, (Lebednik and Palmisano 1977). In this study, some *Alaria fistulosa* were over 20 m long, and some *Alaria nana* were over 5 m long. Some of the kelp plants persist through the winter, but the blades break off, leaving only the holdfasts (Lebednik and Palmisano 1977) and stipe. We counted 15 growth rings on some of the *Laminaria* stipes (Burger, unpublished data).

Kelp and other algae also form part of a subsistence diet for many Native Alaskans (Garza 2005), including the Unangan peoples living in the Aleutians. There are many recipes for *Ulva*, *Fucus*, *Alaria* and other common algae (Garza 2005). Marine algae products are also used extensively in the human diet in other places, particularly in the Arctic (Chan et al. 1995), in Canada (Sharp et al. 1988), and in Asian countries (Phaneuf et al. 1999; vanNetten et al. 2000). In some Arctic communities, kelp contributes significantly to the total metal intake (Chan et al. 1995). Recently, dried and tablet algae has appeared in health food stores in North America (vanNetten et al. 2000). Marine algae is also used as feed for livestock, for soil manure, for abstracting iodine, and for colloid production (e.g. in agar, Caliceti et al. 2002).

2 Materials and Methods

Adak Island, located approximately 1,900 km west of the tip of the Alaskan Peninsula, is in the central Aleutian Chain (Fig. 1). Established as a National Wildlife Refuge in 1913 by executive order of President Taft (ATSDR 2002), the Aleutian Islands separate the Pacific Ocean from the Bering Sea. From 1942 until 1997, a Naval Air Facility occupied the northeastern portion of the island (ATSDR 2002). Over 100,000 military personnel were stationed on the island during the peak years, creating the potential for contamination of the marine environment, particularly near the seaport and airport areas of Akak. In 1994 the Naval Air Station at Adak was placed on the National Priority List based after an EPA RCRA inspection (ATSDR 2002). The airbase closure beginning in 1997 included extensive cleanup. Currently most of the 150 to 200 people on the island reside in the town of Adak, which has an airport and seaport. The island is partly owned by the Aleut Corporation, which is in the process of developing commercial fisheries, and partly by the U.S. Fish and Wildlife Service.

Kelp were collected under appropriate permits from the State of Alaska's Department of Fish and

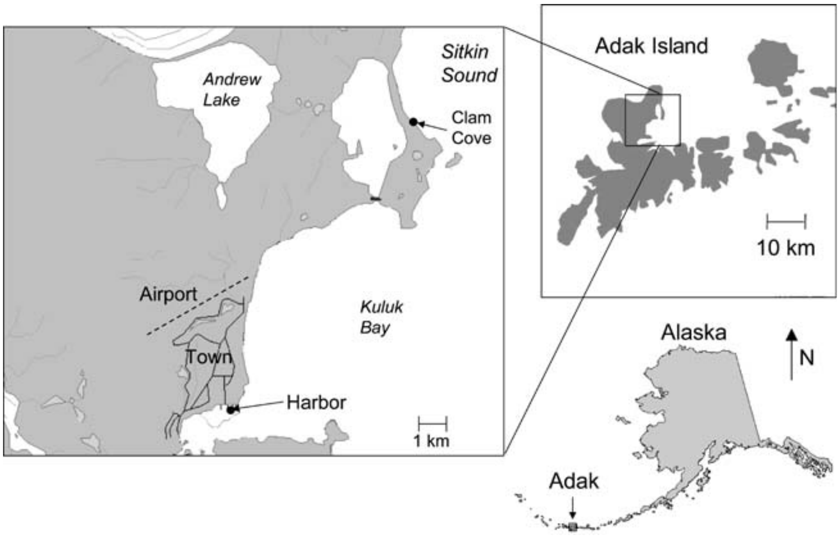

Fig. 1 Location of Adak Island in the Aleutian chain of Alaska in the Northern Pacific/Bering Sea ecosystem

Game (# CF-04-043) and from the native corporation on Adak. Samples were taken from Adak harbor and from Clam Cove. Adak Harbor opens into Kuluk Bay, which in turn opens to the Pacific Ocean and Bering Sea; Clam Cove opens to the Bering Sea. Cold-water wet suits were required for collecting the algae from rocks submerged during most tides. In our temporary laboratory on Adak, kelp were weighed and measured, and the following parts removed, weighed, and placed in plastic bags for freezing: Holdfast, stipe, sporophyte, mid-length of blade (about 50 cm), and tip of blade (*ca* 50 cm). Methods papers for algae, such as White and Gadd (1995) devote considerable attention to the appropriate instrumentation and procedures, as well as the structural location within the cell, but do not address the problem of where on the plant to sample for large algae, such as *Cymathere (=Laminaria)* or *Alaria*. Others have devoted attention to digestion techniques for algae (Pourian and Smith 1974), but did not deal with specific parts either.

Kelp were shipped frozen to the Environmental and Occupational Health Sciences Institute (EOHSI) of Rutgers University for metal analysis. At EOHSI, a 1 g (dry weight) sample of kelp tissue was digested in ultrex ultrapure nitric acid in a microwave (MD 2000 CEM), using a digestion protocol of three stages of ten min each under 50, 100 and 150 lb in^{-2} (3.5, 7, and 10.6 kg/cm^2) at 80× power. Digested samples were subsequently diluted in 25 ml deionized water. All laboratory equipment and containers were washed in 10% HNO_3 solution and deionized water rinse, prior to each use (Burger et al. 2001).

Mercury was analyzed by the cold vapor technique using the Perkin-Elmer mercury analyzer (FIMS 100), with an instrument detection level of 0.2 ppb, and a matrix level of quantification of 0.002 ppm. All other metals were analyzed with graphite furnace atomic absorption (GFAA), including arsenic, cadmium, chromium, lead, manganese, and selenium. Instrument detection limits on the GFAA were 0.2 ppb for arsenic, 0.1 ppb for cadmium, 1.0 ppb for chromium, 2.0 ppb for lead, 1.0 ppb for manganese, and 0.5 ppb for selenium. Matrix detection levels were about an order of magnitude higher. All concentrations are expressed in parts per million (ppm = ug/g) on a wet weight basis. A DORM-2 Certified dogfish tissue was used as the calibration verification standard. Recoveries between 90–110% were accepted to validate the calibration. All specimens were run in batches that included blanks, a standard calibration curve, two spiked specimens, and one duplicate. The accepted recoveries for spikes ranged from 85% to 115%; no batches were outside of these limits. Ten percent of samples were digested twice and analyzed as blind replicates (with agreement within 15%). For further quality control on mercury, our laboratory periodically runs a random subset of samples in the Quebec Laboratory of Public Health; the correlation between the two laboratories is over 0.90 ($P < 0.0001$, see Burger and Gochfeld 2004a).

Multiple regression procedures (PROC GLM, SAS 1995) were used to determine if location (Clam Cove VS. Harbor), part (holdfast, stipe, sporophyte, mid-blade, tip of blade), total length, or interactions between variables, contributed to explaining the variations in metal levels. The procedure adds the variable that contributes the most to the R^2, then adds the next variable that increases the R^2 the most, continuing until all significant variables are added. Thus variables that vary co-linearly are entered only if they add independently to explaining the variation. We used Kruskal Wallis non-parametric one way analysis of variance (generating a X^2 statistic) to examine differences between locations and among parts of the kelp. We also used ANOVA with Duncan Multiple Range test to identify the significant differences (SAS 1995). Kendall correlations were used to examine relationships among metals. The level for significance was designated as $P < 0.05$.

3 Results

Regression models indicated that between 14% (mercury) and 43% (manganese) of the variance in the levels of all metals (except lead) was explained by total length, part of the *Alaria*, and location (Table 1). Interaction variables did not contribute markedly to explaining in metals levels in regression models, and are not considered further. The most significant factor explaining variations in metals levels was *Alaria* length for arsenic and selenium, part for cadmium, chromium and manganese, and location for mercury (Table 1).

The *Alaria* were significantly longer at Clam Cove compared to the Adak harbor (Table 2). There were significant locational differences only for mercury and

Table 1 Models explaining variation in metal levels in *Alaria nana* collected on Adak Island, 2004

	Arsenic	Cadmium	Chromium	Lead	Manganese	Mercury	Selenium
Model							
F	5.7	3.3	3.1	1.1	11.5	2.5	5.0
P	<0.0001	0.006	0.008	0.39	<0.0001	0.03	0.002
r^2	0.27	0.18	0.17	0.07	0.43	0.14	0.25
Factors entering (F, p)							
Length (cm)	15.2 (0.0002)	2.8 (NS)	2.1 (NS)	1.1 (NS)	3.8 (0.05)	0.2 (NS)	5.2 (0.03)
Part	4.7 (0.002)	3.9 (0.006)	4.1 (0.004)	0.8 (NS)	15.8 (<0.0001)	0.8 (NS)	0.6 (NS)
Location	8.8 (0.004)	0.3 (NS)	1.1 (NS)	0.01 (NS)	6.1 (0.02)	6.2 (0.01)	1.3 (NS)

NS Not significant; Interaction variable only entered when it was significant.

selenium (Table 2). Clam Cove had higher levels of selenium and the lower levels of mercury, as well as having the longest kelp. The holdfast had the highest levels for all metals where there was a significant difference in the amounts among parts, although the differences were not great (Table 3).

In general, only mercury and selenium were correlated with the length of the *Alaria* (Table 4). Mercury levels were negatively correlated with length for the mean value for all parts taken together (r = −0.33), and selenium levels were positively correlated (r = +0.37). Manganese levels were also negatively correlated with length for the stipe of *Alaria*.

4 Discussion

4.1 Factors affecting variations in metal levels in the Aleutians

Length, location, and part accounted for variation in metal levels for *Alaria* from the Aleutians. Length was a significant variable only for arsenic, manganese and selenium. This was not due to location because the interaction variable of length with either location or part did not enter the regression models as a significant variable. *Alaria* were longer at Clam Cove compared to the Adak harbor, which may have been due to the physiognomy of the two study sites. The intertidal slope was steeper at the Adak harbor, while it was more gradual at Clam Cove.

For *Alaria*, there were locational differences only for selenium and mercury; mercury was higher in the harbor and selenium was higher in Clam Cove. In a related study of blue mussels (*Mytilus trossulus*), chromium and manganese were higher at Clam Lagoon beach than at the harbor, and mercury was higher in the harbor (Burger and Gochfeld in press). Thus the two studies both found higher levels of mercury in the harbor than at Clam Cove. We had predicted that metal levels in *Alaria* should be highest in the harbor, where both natural currents and direct deposition from ship and land-based runoff occurs, and lowest at Clam Cove by the Bering Sea where direct human impacts appeared less. The town is smaller than it once was; the current population less than 200 compared with over 100,000 military personnel during the peak years. Clam Cove has no

Table 2 Contamininant levels in *Alaria nana* samples collected from from Adak during the summer of 2004

All parts	Clam cove $n=10$	Harbor $n=10$	X^2 (p)	Overall $n=20$
Length (cm)	281.3 ± 18.1	51.1 ± 2.3	73.7 (<0.0001)	167.4 ± 14.8
Arsenic	29.6 ± 1.9	29.3 ± 1.9	0.2 (NS)	29.4 ± 1.3
Cadmium	0.8 ± 0.1	0.6 ± 0.06	0.4 (NS)	0.7 ± 0.07
Chromium	1.6 ± 0.3	1.7 ± 0.3	0.05 (NS)	1.6 ± 0.2
Lead	1.2 ± 0.2	0.8 ± 0.2	0.6 (NS)	1.0 ± 0.1
Manganese	23.7 ± 4.2	18.3 ± 2.0	0.3 (NS)	21.0 ± 2.3
Mercury	0.02 ± 0.009	0.08 ± 0.01	29.8 (<0.0001)	0.05 ± 0.01
Selenium	8.5 ± 1.8	0.09 ± 0.04	33.2 (<0.0001)	4.4 ± 1.0

Given are parts per million, dry weight. Kruskal-Wallis chi square (p).

Table 3 Contamininant levels in five parts (tip, blade, sporophyte, stipe, and holdfast) of 20 *Alaria nana* samples collected equally from from Adak during the summer of 2004

	Tip	Blade	Sporophyte	Stipe	Holdfast	X^2 (p)
Arsenic	27.4 ± 3.5 (B)	26.7 ± 1.6 (B)	23.8 ± 3.1 (B)	30.6 ± 1.9 (B)	38.7 ± 3.5 (A)	13.4 (0.01)
Cadmium	0.6 ± 0.2 (B)	0.6 ± 0.1 (B)	0.8 ± 0.2 (A, B)	0.4 ± 0.1 (B)	1.1 ± 0.2 (A)	9.2 (0.06)
Chromium	1.2 ± 0.2 (B,C)	1.2 ± 0.3 (B,C)	0.7 ± 0.1 (C)	2.1 ± 0.6 (A,B)	2.9 ± 0.6 (A)	12.9 (0.01)
Manganese	14.8 ± 1.9 (B)	15.4 ± 2.5 (B)	15.5 ± 2.4 (B)	9.8 ± 1.4 (B)	49.4 ± 8.2 (A)	28.9 (<0.0001)

Given are parts per million, wet weight. Different letters across rows show significant differences.

nearby habitation, industry, or other activities that might result in direct anthropogenic sources.

In 1994 the Naval Air Station at Adak was placed on the National Priority List based after an EPA RCRA inspection (ATSDR 2002). Metal debris was evident at many places along the harbor, along with oil slicks, and Adak is a still a functioning active harbor. Past contamination, much of which has been remediated, may explain some of the differences. The consistently higher finding for mercury in *Alaria* and mussels from the harbor might reflect this pollution.

However, the relatively high levels of selenium in Clam Cove compared to the harbor were unexpected. In planning the study we had considered Clam Cove a reference site, but the high levels of some metals in kelp and also in blue mussels (Burger and Gochfeld in press) prompted us to do more intensive historical review which revealed a buried landfill within 1 km of the Clam Cove collection site, on the Clam Lagoon causeway (ATSDR 2002; U.S. Navy 2005). Although we did not detect surface evidence of the landfill, which was not excavated but was covered in place, it might partially account for our findings.

Finally, levels were higher in the holdfast for several metals. *Alaria nana* in the Aleutians generally exhibits an annual growth form. Few *Alaria* overwinter, and those that do retain mainly the holdfast since the blade is buffeted and torn by intense winter wave action (Lebednik and Palmisano 1977). While the holdfast can be several years old, the blade is normally regrown each year, and reflect exposure during the growing season. For some algae, metal concentrations vary in different portions of the plant; levels are higher in older parts of the algae (Black and Mitchell 1952; Bryan 1969, 1971; Bryan and Hummerstone 1973; Fuge and James 1973, 1974; Young 1975; Phillips 1990). However, several authors found no differences in different parts of algae (Ray et al. 1980; Sanchiz et al. 1999).

4.2 Comparison with other algae from elsewhere

One of the difficulties of comparing metal levels of *Alaria nana* with other species is the vast number of algae species available for analysis, as well as a lack of consistency in what elements are examined, and

Table 4 Correlations of length with metals in different parts of *Alaria nana* from Adak, Alaska

Length with:	Holdfast	Stipe	Sporophyte	Mid-blade	Tip of blade
Arsenic	NS	NS	NS	NS	NS
Cadmium	NS	NS	NS	NS	NS
Chromium	NS	NS	NS	NS	NS
Lead	NS	NS	NS	NS	NS
Manganese	NS	−0.4 (0.006)	NS	NS	NS
Mercury	−0.4 (0.02)	−0.3 (0.08)	−0.5 (0.003)	NS	−0.3 (0.06)
Selenium	0.3 (0.07)	0.4 (0.01)	0.6 (0.0006)	0.3 (0.09)	0.3 (0.06)

Given are Kendall-tau (p). *NS* Not significant.

the use of wet or dry weight. Further, mercury is often not examined with ICPMS, the usual instrument for analysis of a broad range of elements in algae. Because of the importance of marine algae as food or food supplements, some studies have focused on micronutrients rather than trace contaminants. For example, Hou and Yan (1998) examined 33 elements in 35 marine algae from China, but did not include lead, cadmium, or mercury, the three elements of major concern in oceanic waters (Fowler 1990). Similarly, Blackmore (1998) measured trace metal pollution in several species of algae in Hong Kong, but did not measure mercury. Some comparisons, however, are possible.

At Adak, arsenic levels averaged 29.4 ppm (dw), which was within the range reported for Venice Lagoon (Italy, 7–242 ppm, Caliceti et al. 2002). In Baja California (Mexico), arsenic levels in a wide range of algae varied from 1.5 to 41.1 ppm, but in the Mediterranean Sea, some algae had arsenic levels as high as 93.2 ppm (Al-Masri et al. 2003). Thus the levels at Adak are within the range of these latter values.

Cadmium levels are often high in marine organisms (Bull et al. 1977; Fowler 1990; Furness 1996), especially in kelp (Chan et al. 1995). Further, there is atmospheric deposition (Gao 2001). Cadmium levels in *Laminaria* spp can be 22 times higher in some places than others, mainly due to industrial pollution (Sharp et al. 1988). In this study, cadmium levels averaged 0.7 ppm (dw), which was within the range of the values reported for British Columbia (mean of 0.10 to 2.80 ppm, vanNetten et al. 2000). The levels at Adak were slightly higher than those reported for the Venice Lagoon (Italy, 0.1 to 0.6 ppm, Caliceti et al. 2002) and for Hong Kong (0.48 to 0.78 ppm, Hou and Yan 1998). Levels of cadmium in *Fucus* ranged up to 19.5 ppm in several places in Europe, much higher than in the present study of *A. nana* (Miramand and Bentley 1992).

Chromium levels in Adak (1.6 ppm, dw) were within the range reported for algae from the Venice Lagoon (Italy, means of 0.5 to 4.6 ppm (Caliceti et al. 2002), but lower than China (brown algae, 1.99 ppm, Hou and Yan 1998), and for Baja California (Mexico, 1.73 to 36.2 ppm, Sanchez-Rodriguez et al. 2001), and for several places in Europe (up to 10 ppm, Miramand and Bentley 1992). Chromium levels in algae from the Mediterranean ranged as high as 775 ppm (Al-Masri et al. 2003).

Lead levels at Adak averaged 1.0 ppm (dw). In British Columbia, lead levels in a wide range of algae ranged from 0.08 to 0.58 ppm (vanNetten et al. 2000). Lead levels ranged from 1.6–7.3 ppm (highest levels in *Ulva*) in the Venice Lagoon (Italy, Caliceti et al. 2002), up to 250 ppm in Europe (Miramand and Bentley 1992), and from 1.56 to 37.6 ppm in Hong Kong (Blackmore 1998). Thus the levels of lead from Adak are at the low end of values reported from elsewhere.

There are surprisingly few data on levels of manganese, mercury and selenium in brown algae. Manganese levels ranged up to 166 ppm in algae in Hong Kong (Hou and Yan 1998), compared to 21 ppm at Adak. Mercury ranged from 0.05 to 1.08 ppm in British Columbia in a wide range of algae (vanNetten et al. 2000), compared to 0.05 ppm (dw) at Adak. The lack of mercury data in kelp is surprising given its use as a human food, and bears further examination.

In Baja California (Mexico), selenium levels in a wide range of algae varied from 0.08 to 0.86 (Sanchez-Rodriguez et al. 2001), however, selenium levels were non-detect in Hong Kong (Hou and Yan 1998), and were 4.4 ppm at Adak. Thus, selenium levels in *Alaria* were higher than elsewhere (which would provide added protection from mercury exposure, Ringdal and Julshamn 1985).

Overall, the data indicate that most levels of metals in Adak kelp are within the range reported for other places in the world, including places where algae are harvested extensively for food and fodder. Some of these metals showed a decreasing trend outward from an industrial sources (Caliceti et al. 2002), which is not surprising. At Adak, however, the site expected to be less polluted (Clam Cove, far from town) had higher levels of selenium than in *Alaria* than did the harbor.

4.3 Use of *Alaria nana* as a bioindicator

It is likely that the metals in the *Alaria* examined derive from exposure to water, and not to the sediment, since the holdfast is merely for attachment. This was confirmed by Sanchez-Rodriguez et al. (2001) who found a correlation between a wide range of elemental concentrations in algae of the North Pacific and average elemental concentrations in oceanic waters. Jackson (1998) noted that relatively little is known about the trophic transfer of metals to algae.

There are three potential problems for using *Alaria* as a bioindicator: 1) variations due to season, 2) variations due to different parts of the kelp plant, and 3) variations due to kelp length. Seasonal variation was not great in *Ulva* and other algae in some studies (Haritonidis and Malea 1995), while other studies found seasonal effects in some metals, but not others (Miramand and Bentley 1992; Hou and Yan 1998). In any case, the differences were not great in these studies, and the differences can be mitigated by collecting algae at the same time each year.

Considering variability within a plant or in plants of different age is potentially important, and has been mentioned above (Black and Mitchell 1952; Bryan 1969, 1971; Bryan and Hummerstone 1973; Fuge and James 1973, 1974; Young 1975; Phillips 1990). Sanchiz et al. (1999) found no differences in different parts of the algae *Calerpa prolifera*. These studies, however, suggest that it is species-specific, and depends upon the growth form and age of the algae (Haritonidis and Malea 1995).

Alaria nana in the Aleutians generally exhibits an annual growth form. Some *Alaria* overwinter, and those that do retain mainly the holdfast since the blade is buffeted and torn by intense winter wave action (Lebednik and Palmisano 1977). While the holdfast had significantly higher levels of some metals, the differences were not great, and again, for use as a bioindicator the differences can be mitigated by always collecting the same part of the algae plant.

In this study, there were locational differences in levels of mercury, and selenium, indicating the ability of this species to act as a bioindicator of metals level differences geographically, if they are present. This species of kelp, however, can grow quite long, creating difficulties during collection, sample preparation, and analysis. That is, a 10–20 m long kelp is difficult to collect, hard to dislodge from the bottom, and nearly impossible to homogenize and prepare for analysis. Thus, only some of the plant can be collected and prepared for analysis. The question arises as to whether all parts are equal, or whether samples should be taken from the same place. Length was not correlated with metals levels in any part of the *Alaria*, except for mercury and selenium (and the stipe for manganese). Mercury was negatively correlated with length, and selenium was positively correlated with length. This suggests that to be maximally useful, scientists and managers should develop a consistent protocol, and collect mainly one length for comparison among geographical locations or among years.

4.4 Potential human health and ecoreceptor consequences

One of the difficulties with evaluating the effects of metals on receptors, including humans, is a general lack of consistency across metals, biota, and types of effects (chronic vs acute). That is, the same standard or guideline cannot be found for different metals in a range of different species. In the following discussion, human guideline refers to a value government agencies have derived for safe consumption levels; action level refers to a regulatory level which may or may not be based on consideration of risk from consumption, and effects level refers to a level shown in laboratory experiments to have an adverse effect on reproduction, physiology, or behavior. An adverse effect level can refer either to the level in the diet or in a target organ associated with adverse effects in a given species or species group (such as birds or mammals).

In many places in the world, kelp and other algae are an important human dietary item, and are also fed to livestock (see introduction for references). Thus the metal levels bear examination in terms of health consequences. In this study, arsenic levels averaged 29.4 ppm (dry weight), depending upon the part of the kelp plant examined. Much arsenic in the marine environment is organic arsenic which has relatively low toxicity, but the arsenic in the *Alaria* has not been speciated. In general, effects levels for consumers, including humans, are given in wet weights, which are used in the following discussion.

Adverse effects from cadmium can occur in fish with dietary levels of 0.1 ppm (Eisler 1985). Birds may be less sensitive to cadmium in their diet than mammals, but are adversely affected at levels of 1.0 ppm in their diet (Eisler 1994). Cadmium levels in *Alaria* averaged 0.14 ppm. Thus, there may be some cause for concern for avian predators that eat organisms that feed on kelp. Standards for cadmium in human foods are sparse. Neither the United States nor the United Kingdom have published a standard or an action level for cadmium in algae. The Codex Alimentarius Commission (2002) has standards or proposed standards for cadmium in mollusks

(1.0 ppm) and crustacea (0.5 ppm), but none for algae. For cadmium the Joint Monitoring Programme established under the Oslo and Paris Commissions, set a guideline of 0.2 ppm for fish, and 0.5 ppm for shellfish, but has set no standards for algae (OSPAR (Oslo and Paris Commissions) 1992). The levels of cadmium in *Alaria* at Adak were below these two guidelines.

Chromium levels averaged 0.32 ppm in *Alaria* at Adak. Levels of 10 ppm of chromium in diets are considered to cause adverse effects in some wildlife species, although trivalent chromium is an essential dietary element (Eisler 1986), but there are virtually no guidelines for humans. Similarly, there are remarkably few studies on the dietary effects of manganese on predators. Manganese is an essential trace element, although it can cause toxicity at high doses.

Lead is neurotoxic and nephrotoxic, causes behavioral deficits in vertebrates, and can cause decreases in survival, growth rates, learning and metabolism in a wide range of wildlife species (Eisler 1988; Weber and Dingel 1997; Burger and Gochfeld 2000). Levels of 50 ppm in the diet can cause reproductive effects in some predators, and dietary levels as low as 0.1 to 0.5 ppm are associated with learning deficits in some vertebrates (Eisler 1988). In this study, the levels of lead in *Alaria* averaged 0.2 ppm, suggesting that attention should be devoted to examining lead levels in algae that are eaten in the region, along with consumption patterns. The Codex Alimentarius Commission (2002) specifies a human level for lead in fish (0.2 ppm), and for lead in mollusks (formerly 0.5 ppm but discontinued, Codex Alimentarius Commission 2003), but does not generally do so for most other marine foods. Using this guideline for kelp would suggest caution in consumption of *Alaria* from Adak.

The mercury levels in *Alaria* at Adak averaged 0.01 ppm, well below the 1.0 ppm FDA action level in fish for humans (reviewed in Burger and Gochfeld 2004b), and thus the kelp from either location pose no apparent risk to human consumers from mercury. Likewise, concentrations of 15 ppm are required for adverse effects in predators (Spry and Wierner 1991; Wiener and Spry 1996). However, sensitive birds can exhibit effects at dietary mercury concentrations of 0.05 to 0.5 ppm; for sensitive mammals, harmful effects occur at dietary levels of 1.1 ppm (Eisler 1987; WHO 1990, 1991), although the safe levels for kelp consumption by wildlife are unknown.

The levels of selenium in *Alaria* were 94 times higher at Clam Cove than at the Harbor, certainly an important difference. Although selenium is an essential micronutrient, it can be toxic at high levels in a range of organisms (Coyle et al. 1993). Levels of about 1 ppm, wet weight in food is the threshold for selenium toxicity in some organisms (Lemly 1993a, 1993b). The levels for Clam Cove averaged 1.7 ppm, suggesting that selenium might pose a problem for some organisms that consume *Alaria*, including sea urchins and fish (Lemly 1993a, b). The few international standards for human diets range from 0.3 to 2.0 ppm (see Burger and Gochfeld 2005 for review). The mean levels of selenium in this study exceeded this, suggesting that further study is warranted of both local consumption rates of kelp from Clam Cove, and of levels in other kelp from the area.

Overall, cadmium, lead and selenium had levels that indicating that predators, including people, may be at risk from consuming *Alaria*, at least from Clam Cove. Our results suggest that more attention should be devoted to heavy metal levels in kelp and other algae from Adak, particularly if they are an important part of a subsistence diet on Adak. Future studies should examine heavy metal levels in other species of algae from Adak, and from other islands in the Aleutians with less human impact to determine the potential risk to subsistence consumers, and whether the contaminants reflect regional background or anthropogenic sources. Contaminants data, however, is useful for risk assessment only if there are also consumption data for at risk populations.

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