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Baseline Concentrations of Trace Metals in Macroalgae from the Strait of Magellan, Chile

M[a]. Soledad Astorga-España · Nancy Cristina Calisto-Ulloa · Sandra Guerrero

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Abstract Samples of four different species of seaweed were collected monthly between October 2000 and March 2001 from the coast of the Strait of Magellan, Chile to establish baseline levels of trace metals (silver, total mercury, nickel, lead, antimony, vanadium and zinc) and to compare the accumulation capacity among species. The algae included in the study were *Adenocystis utricularis* (n = 15); *Enteromorpha* sp. (n = 11), *Mazzaella laminarioides* (n = 12) and *Porphyra columbina* (n = 6). The concentration range of each metal in $\mu g\ g^{-1}$ dry weight varied as follows: Ag = ND-0.3, Hg = ND-0.02, Ni = ND-12.6, Pb = ND-11.2, Sb = ND-1.97, V = ND-11.34 and Zn = 14.10-79. Results showed that levels of Ag, Hg, Ni, Pb, Sb, V and Zn for all species were similar to those found in other studies for non-contaminated areas with very little influence from anthropogenic activity. Also among the four species studied macroalgae *Enteromorpha* sp. *had* the highest capacity for metal accumulation and could therefore be considered as a biomonitor for future studies in the area.

Keywords Bioindicators · Metals · Macroalgae · Trace elements

M[a]. S. Astorga-España (✉) · N. C. Calisto-Ulloa
Department of Science and Natural Resources, University of Magallanes, Av. Bulnes, P.O. Box 113-D, 01855 Punta Arenas, Chile
e-mail: msoledad.astorga@umag.cl

S. Guerrero
Center for Environmental Sciences and Engineering, University of Connecticut, 3107 Horsebarn Hill Road, Building 4 Annex, U-4210, Storrs, CT 06269-4210, USA

The use of biological species in the monitoring of marine environmental quality allows the evaluation of the biologically available levels of contaminants in the ecosystem or effects of contaminants on living organisms.

Macroalgae are one the most efficient and reliable indicator organisms used to study trace metal pollution (Phillips 1977). Commonly, marine macroalgae have been used as bioindicators because of their accessibility, presence at sites prone to pollution (e.g., estuaries), longevity, and their benthic nature (Stengel et al. 2004). Seaweeds concentrate metals from solution and integrate short-term temporal fluctuations in concentrations of dissolved metals from the biologically available fraction (Orduña-Rojas and Longoria-Espinoza 2006).

The Strait of Magellan is an important marine transportation channel between the Pacific and Atlantic Oceans, and an important navigation route to Antarctica. In the past, the Strait has been subject to various human activities such as domestic waste discharge without treatment and industrial activities, including discharge from petrochemical industries, petroleum exploitation on offshore oil platforms near the coast, petroleum terminals and accidental oil spills.

It is imperative that the environmental impact of these activities and the effects on organisms be monitored in order to maintain viable ecosystems. However, little trace metal data are available in terms of baseline concentrations in marine organisms from the Strait of Magellan (Astorga España et al. 2004, 2005), while there is no information about heavy metals levels in algae.

Thus, the objective of this study was to determine the concentration of heavy metals in four species of macroalgae: *Adenocystis utricularis*, *Enteromorpha* sp., *Mazzaella laminarioides* and *Porphyra columbina* in the Strait of Magellan. These species were chosen due to the fact they are widely used as bioindicators of metal contamination (Buo-Olayan and Subrahmanyam 1996; Brown et al. 1999; Villares et al. 2002). Besides their widespread distribution in the Strait's coastal areas, these species meet some additional criteria as ideal biomonitors including being sessile or sedentary and easy to sample.

Materials and Methods

San Juan, Fig. 1, located 70 km southeast of Punta Arenas, Chile (53°37′ S, 70°59′ W), was selected as the study site due to its pristine environment and limited anthropogenic activity. Forty four samples of seaweed (*A. utricularis.*, n = 15; *Enteromorpha* sp., n = 11; *M. laminarioides*, n = 12; and *P. columbina*, n = 6) were collected monthly between October 2000 and March 2001. Intertidal benthic macro-algae were randomly collected at low tide by hand from the surface of beach rocks, washed with seawater from the sampling site and stored in acid-cleaned plastic bags. Samples were transported in coolers with ice to the laboratory. Once at the laboratory, samples were washed with Milli-Q deionized water to remove epiphytes, salt and foreign particles. Samples were dried at room temperature overnight, and then in an oven at 60°C until weight was constant. They were then homogenized and kept away from possible sources of contamination. Samples were analyzed at the Center for Environmental Sciences and Engineering at the University of Connecticut, USA. Generally metals concentrations vary in different portions of a plant, with higher concentrations found the older parts as compared to the younger parts such as growing tips (Farias et al. 2002). In this study, only whole plants were analyzed in order to obtain information about the mean concentration of trace metals.

Samples were digested using EPA method 200.3 (US EPA 1991). The analysis of nickel (Ni), vanadium (V), and zinc (Zn) was done by Inductively Coupled Plasma-Atomic Emission Spectroscopy according to EPA method 6010B (US EPA 1996) using a Perkin–Elmer Optima 3300XL. Silver (Ag), lead (Pb), and antimony (Sb) were analyzed by Inductively Coupled Plasma-Mass Spectroscopy according EPA method 6020 (US EPA 1994) using a Perkin–Elmer Sciex Elan 6000. Samples for total mercury (Hg) analysis were digested and analyzed according EPA method 245.6 (US EPA 1991) using a Perkin–Elmer FIMS-FIAS 100, Cold Vapor Atomic Absorption System. The accuracy of the method was verified by analysis of NRC Standard Reference Material, DORM-2 and DOLT-2 (dogfish muscle and liver) showing recoveries >95% for Zn and between 85% and 89% for Ag, Pb, Ni and Hg. The detection limits (μg g^{-1}, dry weight) for each element were as follows: Ag = 0.02, Pb = 0.5, Ni = 1.0, V = 1.2, Zn = 2, Hg = 0.01 and Sb = 0.2.

Means and standard deviations were calculated for each element and each algae. Where less than 60% of samples were non-detects (ND), a value of one-half the detection limit was substituted for each ND (Clarke 1998). Where greater than 60% of samples were ND, the proportion of samples below detection was presented in place of the mean (Clarke 1998).

Results and Discussion

Table 1 shows detection limits, ranges, number of samples and means ± 1 standard deviation for the trace metal analysis of four species of algae collected at San Juan station, in the Strait of Magellan, Chile. The concentration range of each metal in μg g^{-1} dry weight varied as follows:

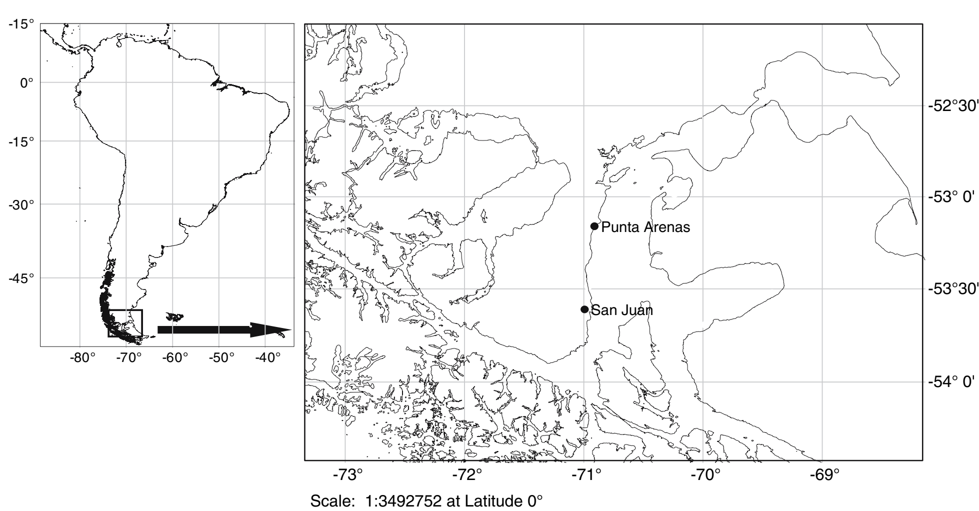

Fig. 1 Sampling site San Juan in Strait of Magellan, Chile

Table 1 Concentrations of metals (μg g^{-1} dry weight) in the samples of macroalgae

Analyte	DL[a]	*A. utricularis*	*Enteromorpha* sp.	*M. laminarioides*	*P. columbina*
Ag					
	0.02	ND-0.10 (*n = 15*)	ND-0.10 (*n = 11*)	ND-0.30 (*n = 12*)	ND-0.20 (*n = 6*)
		67% < DL	***64% < DL***	***0.07 ± 0.09*** (*)	***83% < DL***
Hg	0.01	ND (*n = 10*)	ND-0.02 (*n = 7*)	ND (*n = 7*)	ND (*n = 4*)
		100% < DL	***71% < DL***	***100% < DL***	***100% < DL***
Ni	1	ND-1.00 (*n = 15*)	ND-12.60 (*n = 11*)	ND-7.60 (*n = 12*)	ND-2.60 (*n = 6*)
		93% < DL	***2.67 ± 3.51*** (*)	***67% < DL***	***83% < DL***
Pb	0.5	ND-2.02 (*n = 15*)	ND-11.20 (*n = 11*)	ND-7.40 (*n = 12*)	ND-8.20 (*n = 6*)
		67% < DL	***2.08 ± 3.15*** (*)	***67% < DL***	***83% < DL***
Sb	0.2	ND-0.89 (*n = 15*)	ND-1.97 (*n = 11*)	ND-1.02 (*n = 12*)	ND-0.80 (*n = 6*)
		87% < DL	***72% < DL***	***92% < DL***	***67% < DL***
V	1.2	ND-3.71 (*n = 10*)	ND-11.34 (*n = 7*)	ND-4.43 (*n = 7*)	ND-3.08 (*n = 4*)
		80% < DL	***3.94 ± 3.97*** (*)	***3.78 ± 0.57*** (*)	***2.60 ± 0.51*** (*)
Zn	2	14.1–32.3 (*n = 5*)	17.2–79.7 (*n = 4*)	28.0–67.2 (*n = 5*)	20.4–23.4 (*n = 2*)
		22.18 ± 6.74	***35.80 ± 29.94***	***41.74 ± 15.70***	***21.90 ± 2.12***

[a] DL = Detection limit

(*) = ND replaced by ½ DL

Range, number of samples (italics, in parentheses), and means ± 1 standard deviation (bold italics) of metals concentrations. Where >60% of samples were below detection (ND), the percent of samples below the detection limit (DL) was used in place of the mean

Ag = ND-0.3, Hg = ND-0.02, Ni = ND-12.6, Pb = ND-11.2, Sb = ND-1.97, V = ND-11.34 and Zn = 14.10-79.

As expected, Zn showed the highest concentrations and the widest range for all species studied (Table 1). In contrast, the percentage of ND samples for Hg was 100% for all species except for *Enteromorpha* sp. (Table 1). There were also a large percentage of samples below detection for Sb, Ag, Pb, and Ni (Table 1). Besides Zn, V was the most abundant element in this study, with mean concentrations of 3.94, 3.78 and 2.6 (μg g^{-1}) dry weight for *Enteromorpha* sp., *M. laminaroides* and *P. columbina*, respectively. In general, *Enteromorpha* sp. was the algae with the most quantifiable concentrations (Table 1). The other species had large numbers of samples below detection for most metals measured (Table 1).

Green algae are considered a bioindicator of contamination (Brown et al. 1999). In this particular study a mean concentration for Zn of 35.8 μg g^{-1} dry weight was found (Table 1) for the green algae *Enteromorpha* sp. This value is within the range of 10–50 μg g^{-1} Zn dry weight considered characteristic for a non-contaminated area, and below the range of 95–130 μg g^{-1} Zn dry weight, considered characteristic of a contaminated area (Brown et al. 1999). Also, the highest mean concentration of Zn determined for the red algae *M. laminarioides* of 41.76 μg g^{-1} dry weight is within the range considered free of contamination.

Say et al. (1990) proposed three concentration ranges of Zn in *Enteromorpha* as an indication of the degree of contamination within estuaries: <50 μg g^{-1} dry weight for an uncontaminated area, 50–150 μg g^{-1} dry weight for moderate contamination and >150 μg g^{-1} dry weight for high contamination. The mean Zn concentration in all algae examined in this study were <50 μg g^{-1} dry weight (Table 1).

The *Enteromorpha* used in the present study are amongst the most commonly used genus in the biomonitoring of trace metal pollution. Different species of algae of the genera *Enteromorpha* have been used as bioindicators of contamination in different parts of the world (Buo-Olayan and Subrahmanyam 1996; Brown et al. 1999; Villares et al. 2002). Other studies using *Ulva lactuca*, *Enteromorpha prolifera* and *Porphyra columbina* as bioindicators had been done by Muse et al. (1999) in the Gulf San Jorge, Argentina, to investigate a digestion method of metals using a microwave for the determination of Zn, Cu, Cr, Pb and Cd. According to several authors (Villares et al. 2002; Buo-Olayan and Subrahmanyam 1996), levels of metals in macroalgae vary depending on several environmental factors such as salinity, nutrients, pH, age of the plant, season of sampling and analytical methods used for the quantification. Therefore, caution should be used when comparing metals levels between distant areas with very different characteristics. However, since there have not been other studies of metals in algae from the San Juan zone or other areas near the Strait of Magellan, the results for the *Enteromorpha* sp. from this study (Pb, Ni, and V only) are compared here with other published results for the same genus, to determine if values of the present study belong to a zone free of contamination. Buo-Olayan and Subrahmanyam (1996) reported a mean concentration of 8.5, 7.1, 8.5 μg g^{-1} dry weight for Pb, V and Ni, respectively in *E. intestinales* and 6.5, 10, 9.1 μg g^{-1} dry weight for *E. flexuosa* from the Kuwait coast, an area considered contaminated due high levels of metals found in previous studies of sediments and water. The concentrations of Pb, V, and Ni (2.08, 3.94 and 2.67 μg g^{-1} dry weight, respectively) found in the present study were lower than those from the Kuwait coast; concentrations were approximately three times less for Pb and Ni, and nearly one half the value for V. Pb concentrations in *Enteromorpha sp* found in the present study (2.08 μg g^{-1} dry weight) were only slightly higher than the 1.81 μg g^{-1} dry weight reported for *E. prolifera* near the coast of the Adriatic Sea in Italy, which is an area considered free of contamination (Storelli et al. 2001). Levels of V in *A. utricularis* from Antarctica (Farias et al. 2002) were 3.99 μg g^{-1} dry weight, which is very similar to the V concentration for *Enteromorpha sp* in the present study (3.94 μg g^{-1} dry weight). It was not possible to compare between the same species of algae (*A. utricularis*), due to the large number of samples below detection (80%). In the Agibampo lagoon on the Pacific coast of Mexico, an area considered to be free of contamination, a Ni concentration of 3.7 μg g^{-1} dry weight was reported for *E. linza* (Páez-Osuna et al. 2000). This value was higher than the 2.67 μg g^{-1} dry weight concentration of V found for *Enteromorpha* sp. in the present study.

It is also important to consider that whenever the authors report values for concentration of metals from areas defined as contaminated does not necessarily mean that there are important amounts of all the metals quantified in the area, because high concentration levels of one metal in particular will depend on the anthropogenic activity near the area of study (Villares et al. 2002). Different algae exhibit different affinities towards different metals, which in turn depend on the chemical structure of the biosorbent (Hamdy 2000). Also, metal concentrations vary in different portions of the plant, being generally higher in the older parts of the algae and lower in fast growing tips, as the older parts of the plants are exposed to the ambient concentration of element for a longer time than younger parts (Farias et al. 2002). In this study, only whole organisms were analyzed in order to obtain information about the mean concentration of trace metals in algae. Despite the fact that all species were collected under the same conditions, only the macroalgae *Enteromorpha* sp. were found to have a higher capacity to accumulate metals among the four species analyzed. Therefore, it is suggested to consider *Enteromorpha* sp. as a biomonitor in future studies of metals in the area.

In addition, it is known that contaminants such as heavy metals occur naturally in the environment and it is important to be able to distinguish between anthropogenic contamination and background or natural levels to enable accurate evaluation of the degree of contamination an area (Villares et al. 2002).

Levels of Ag, Hg, Ni, Pb, Sb, V and Zn determined in the present study for *A. utricularis*, *Enteromorpha* sp., *M. laminarioides* and *P. columbina* from San Juan area of the Strait of Magellan can be considered as normal values for algae from that area, and therefore can be taken as base value for future studies, especially because the San Juan area is an area with very little anthropogenic activity. The chosen area displays an easy access, as well as a high biodiversity and abundance of macroalgae which constitutes important advantages with respect to other sectors of the Strait of Magellan, which do not show contamination by metals according to previous studies (Astorga España et al. 2004, 2005) even though are exposed to different degrees of human activities.

Where direct comparisons could be made, metals concentrations found in this study were similar to those found in other studies for non-contaminated areas. Although the presence of large numbers of samples with ND values makes direct comparisons with literature values difficult, the findings still provide valuable information. Large numbers of samples below detection limits support the premise that the area of sampling used in the present study shows very little influence from anthropogenic activity.

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