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Mercury content in intertidal algae from La Caleta de Interián, North coast of Tenerife, Canary Islands

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Summary
Mercury content in intertidal algae from La Caleta de Interián, North coast of Tenerife, Canary Islands.
An analysis of Hg content was performed by sampling three species of algae, *Ulva rigida C.Agardh*, 1823, *Cystoseira abies-marina* (S.G. Gmelin) *C.Agardh*, 1820 and *Corallina sp*, from the intertidal coastal waters of La Caleta de Interián. The minimum concentration found was 0.1 mg/kg in *C. abies-marin*a and the maximum was 0.15 mg/kg in *U. rigida.* Significant differences in Hg were observed in *U. rigida*, *C. abies-marina* and *Corallina. sp*., whose Hg concentration was lower than that in Ulva. A comparison of the data with other studies about the island of Tenerife shows that the concentrations of Hg have not changed over time in this locality. The data reported in the study confirms that the algae are within a range suitable for human consumption according to the ADI (Admissible Daily Intake).
Keywords: *Ulva rigida*, *Cystoseira abies-marina*, *Coralina abies marina*, Hg, ADI and human consumption.

Resumen
Contenido de mercurio en algas intermareales de La Caleta de Interián, costa norte de Tenerife, Islas Canarias.
Se realizó un análisis del contenido de Hg muestreando tres especies de algas, *Ulva rigida C.Agardh*, 1823, *Cystoseira abies-marina* (S.G. Gmelin) *C.Agardh*, 1820 y *Corallina sp*, de las aguas costeras intermareales de La Caleta de Interián. La concentración mínima encontrada fue de 0,1 mg / kg en *C. abies-marina* y el máximo fue de 0,15 mg / kg en U. rigida. Se observaron diferencias significativas en Hg en *U. rigida*, *C. abies-marina* y *Corallina. sp*., cuya concentración de Hg fue menor que la de Ulva. Una comparación de los datos con otros estudios en la isla de Tenerife muestra que las concentraciones de Hg no han cambiado con el tiempo en esta localidad. Los datos informados en el estudio confirman que las algas se encuentran dentro de un rango adecuado para el consumo humano según la IDA (ingesta diaria admisible).
Palabras clave: *Ulva rigida*, *Cystoseira abies-marina*, *Coralina abies marina*, Hg, ADI y consumo humano

Introduction

The levels of pollution in aquatic systems and the induced impacts on living organisms have long been a subject of research [17]. In these ecosystems, metals are among the most common contaminants, with several studies showing high concentrations in sediments, water and organisms and their deleterious effects at various biological levels. The concentrations of metals in seawater are very low and show wide fluctuations [6, 14].
Mercury (Hg) is one of the most toxic elements due to its high persistence, bioaccumulation potential and toxicity [1, 21]. This metal is highly toxic to organisms [18] and Hg contamination has significantly affected ecosystems at local, regional, national, and global levels. Since the 1970s, a number of policies have been enacted in Europe and North America to reduce Hg production and discharge [13, 16]. Since Hg comes from natural and anthropogenic sources, its background level from natural sources is necessary to assess anthropogenic pollution. Muir et al., [19], studied the records of Hg deposition

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in lake sediments in mid- and high-latitude areas and assessed levels of anthropogenic Hg.
Heavy metals in domestic and agroindustrial waste water are also responsible for the pollution of rivers, lakes and seas [8]. Biosorption and accumulation of heavy metal ions in aquatic food chains can pass to humans causing significant health problems [22, 24]. Biosorption is a term that describes the removal of heavy metals by passive attachment to the non-living biomass of an aqueous solution. This implies that the elimination mechanism is not metabolically controlled. In contrast, the term bioaccumulation describes an active process by which the elimination of metals requires the metabolic activity of a living organism. [2, 3, 7]. On an international level, the behaviour of several marine algae has been studied with particular interest as biosorbents of toxic metals, because of their renewable character and low cost, in order to use them in a more economical way than the conventional adsorbents for the large scale treatment effluents [15].
The objective of the present study is to study whether the concentrations of Hg in algae vary according to the species, to determine which species is the better Hg bioaccumulator, to see whether the study area has high levels of Hg concentration and confirm if these algae are suitable for human consumption.

Materials and methods

Field work
A total of three species of algae (*Ulva rigida* C. Agardh, 1823, 15 specimens, *Cystoseira abies-marina* (SG Gmelin) C.Agardh, 1820, 15 specimens, *Corallina sp.*, 15 specimens) were sampled from the coast of La Caleta de Interián on the North coast of Tenerife, Canary Islands (Figure 1). Samples weighing 10 g were taken. Algae were digested using a sulfonitric mixture (HNO_3: H_2SO_4) for 18-24 h at 40°C [9]. After they were completely digested, Hg concentration levels were determined using cold vapour atomic absorption (AAS) spectrophotometry. The Standard Reference Material (CRM 279 *Ulva lactuca*) was analyzed following the same procedure as the samples to control accuracy and precision.
Data analysis
Statistical analysis was performed using the IBM Statistic SPSS 22.0 program. In each analysis, the same procedure was carried out to verify whether the data followed a normal distribution, thus fulfilling normality and homogeneity of variances, using $P < 0.05$. To verify the existence or not of normality in the concentration data of heavy metals, the tests of normality (Test of Kolmogorov-Smirnov) and of homogeneity of the variances (Statistical of Levene) were performed. If the data followed a normal distribution ANOVA was applied, using Tukey's post hoc (since there were more than 2 groups of samples). A Box and Cox transformation was applied to all non-normal data. When carrying out these transformations, the data which still did not show a normal distribution were subjected to non-parametric tests using the Kruskal-Wallis statistical test. Subsequently, if there were statistically significant differences between the data, the Mann-Whitney U test was applied to determine between what types of samples these significant differences existed.

Figure 1: Area of La Caleta de Interián and Faro de Buenavista del Norte, sampling site. ©CabildodeTenerife.

Results

The results shown in Table 1 show the concentration of Hg (mg/kg) for each of the three algae species with the maximum concentration being 0.15 mg/kg in a sample of *Ulva rigida*, and the minimum concentration 0.02 mg/kg in a sample of *Cystoseira abies-marina* (Table 1). A validation study of Hg was performed to check the correctness of the methodology (Table 2)
In the statistical analysis, the variable concentration of Hg meant that it did not follow a normal distribution. Therefore, non-parametric tests were performed, starting with the Kruskal-Wallis test (sig = 0.000). There were significant differences between species, and to check between which species those differences existed, Mann-Whitney's U test was performed (Table 3). There were significant differences between Ulva rigida and Cystoseira abies-marina (sig = 0.001), and between Ulva rigida and Corallina sp. (sig = 0.001). There were no significant differences (sig = 0.473) between Corallina sp. and Cystoseira abies-marina.

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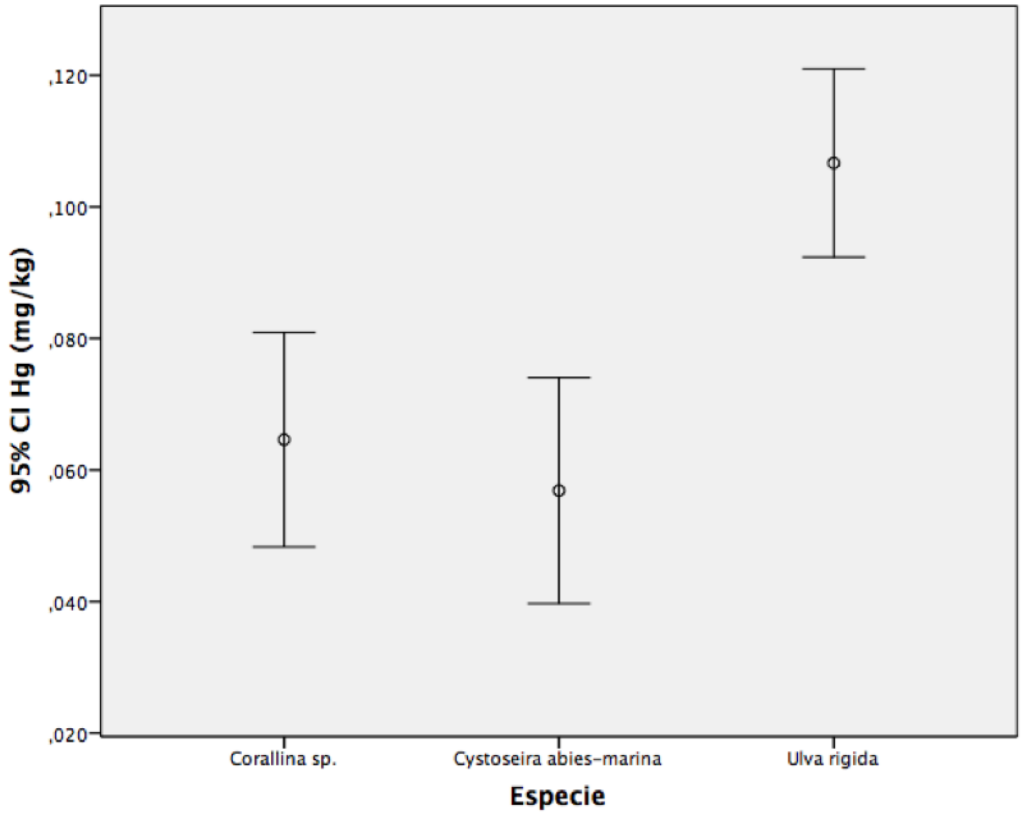

Figure 2: Error bar graph of algal species for Hg concentration (mg / kg), with a 95% confidence interval. The clear difference in the case of Ulva rigida is observed.

Table 1: Concentration of Hg (mg/kg) for each of the algal species.

	Hg (mg/kg)		
	Ulva rigida	*Corallina sp.*	*Cystoseira abies-marina*
1	0.090	0.040	0.020
2	0.110	0.050	0.050
3	0.090	0.040	0.030
4	0.080	0.090	0.070
5	0.140	0.070	0.100
6	0.110	0.070	0.080
7	0.120	0.030	0.110
8	0.120	0.090	0.060
9	0.070	0.030	0.020
10	0.110	0.110	0.070
11	0.150	0.050	0.010
12	0.100	0.070	0.090
13	0.150	0.100	0.060
14	0.080		0.020
15	0.080		0.060
Means	0.107 ± 0.026	0.065 ± 0.027	0.057 ± 0.031

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Table 2: Hg validation study

Metal	Material	No. samples	Means (mg/kg)	Certified	Process
Hg	CRM 279 *Ulva lactuca*	43	0.193 ± 0.009	0.195 ± 0.010	EAA with Hydride Generator

Table 3: Mann-Whitney U analysis for each species of alga. Significant values (p = 0.005).

	Ulva rigida	***Corallina sp.***	***Cystoseira abies-marina***
Ulva rigida	------------------------	0.001 *	0.000 *
Corallina sp.	------------------------	------------------------	0.473
Cystoseira abies-marina	------------------------	------------------------	------------------------

Table 4: Values of intakes taking a person of 70 kg as reference. Reference is made in the columns to the species and the weight in kilograms of algae that should be consumed to reach the ADI.

ADI (Hg)	*Ulva rigida*	*Corallina sp.*	*Cystoseira abies-marina*
60 mg/kg/day	3.99	5.55	7.49

Discussion

Comparing the concentrations of Hg in the algae of the present study with the algae from the study of [12], which also sampled in La Caleta de Interián, it was observed that the Hg concentrations of the present study in *Coralina elongata* (0.065 mg/kg) and *Cystoseira abies-marina* (0.057 mg/kg) were higher than those reported by [12], 0.04 and 0.05 mg/kg, respectively. However, the values for *Ulva rigida* (0.107 mg/kg) are lower than those found by the above authors (0.12 mg/kg). It should be noted that only two specimens of each species were sampled at the said location in the article used for comparison.

In the future, a study the degree of biosorption of algae for heavy metals is recommended, since according to [5] this could be the solution for the removal of heavy metals from the marine environment; it would be necessary to study techniques combined with pH [20] and temperature to check whether biosorption is affected by these factors, taking the study of [11] in polychaetes as the reference. The results of the above mentioned study showed that low pH conditions can induce oxidative stress in this group of worms. The study of [4] performed tests with organisms, almost all of which were vegetables, which found that the biosorption of heavy metals noticeably increased at pH 5.

Previous studies have shown that transition heavy metals such as Cu and Hg tend to cause oxidative stress [25]. In the study by [10], it was observed that the growth of green alga *Chlamydomonas reinhardtii* was inhibited by Hg at levels 4-8 mL, where chlorophyll was also found to be less abundant. Toxic symptoms can represent severe stress caused by a relatively higher level of Hg.

The results reported in the present study show that *Ulva rigida* is the alga with the highest Hg content (Figure 2). *Ulva rigida* is a green alga and according to [15] some of the green algae species have a lower detoxification capacity which may explain why *Ulva rigida* contains the highest concentration of Hg.

Observing the data obtained for the comparison with the ADI (Admissible Daily Intake) of Hg (Table 4), it is observed that the three species are far from this control value, a finding that indicates that these algae are not yet contaminated by Hg since 3.99 kg of *Ulva rigida*, 5.55 kg of *Corallina sp*. and 7.49 kg of *Cystoseira abies-marina* would need to be consumed to reach the ADI. Therefore, these algae could be used for human consumption without any risk to human health [23].

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Conclusions

The concentrations of Hg in algae have not undergone many large changes. *Ulva rigida* has the highest Hg content, and this is explained by the low rate of detoxification of green algae.

In the future, a deeper study of the process of bioaccumulation of heavy metals in green algae is recommended as a possible bioremediation of these metals in the oceans.

The three species of algae are not contaminated with Hg when taking into account the ADI of Hg.

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