Journal of the Marine Biological Association of the United Kingdom

cambridge.org/mbi

Research Article

Cite this article: Méndez-Rodríguez L, Piñón-Gimate A, Casas-Valdez M, Cervantes-Duarte R, Arreola-Lizárraga JA (2021). Macroalgae from two coastal lagoons of the Gulf of California as indicators of heavy metal contamination by anthropogenic activities. *Journal of the Marine Biological Association of the United Kingdom* **101**, 1089–1101. https://doi.org/10.1017/S0025315422000182

Received: 7 July 2021
Revised: 18 February 2022
Accepted: 25 March 2022
First published online: 27 April 2022

Key words:
Anthropogenic activities; bioindicator; canneries; coastal lagoons; industries; macroalgae; metals; mining; seasonal variability

Author for correspondence:
Alejandra Piñón-Gimate,
E-mail: ale_pinion@hotmail.com

Macroalgae from two coastal lagoons of the Gulf of California as indicators of heavy metal contamination by anthropogenic activities

Lia Méndez-Rodríguez[1], Alejandra Piñón-Gimate[2], Margarita Casas-Valdez[2], Rafael Cervantes-Duarte[2] and José Alfredo Arreola-Lizárraga[3]

[1]Centro de Investigaciones Biológicas del Noroeste, S.C., Campus La Paz. Av. Instituto Politécnico Nacional 195, Playa Palo de Santa Rita Sur, La Paz, Baja California Sur 23096, México; [2]Instituto Politécnico Nacional, Centro Interdisciplinario de Ciencias Marinas (IPN-CICIMAR). Av. Instituto Politécnico Nacional sn, Playa Palo de Santa Rita Sur, La Paz, Baja California Sur 23096, México and [3]Centro de Investigaciones Biológicas del Noroeste, S.C., Campus Guaymas. Carretera a las Tinajas, kilómetro 2.3, predio El Tular, Guaymas, Sonora 85454, México

Abstract

Metal concentrations in coastal zones are a critical study subject since anthropogenic activities surrounding these zones are increasing and affecting environmental concentrations of metals. Macroalgae have been used as biomonitors since they can act as indicators of metal concentrations in the water column. Tissue samples of three abundant macroalgae species (*Spyridia filamentosa*, *Padina mexicana* and *Ulva ohnoi*) were collected from three sites with different anthropogenic impacts at La Paz Bay and Guaymas Bay, Mexico, during three contrasting seasons (dry, rainy and cold) in the year 2016. Tissue concentrations of iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni), cadmium (Cd) and lead (Pb) were determined by atomic absorption spectrophotometry. The highest concentrations were found in *S. filamentosa* inhabiting both bays. The highest Cd and Mn concentrations were recorded in algae from La Paz Bay, while the highest concentrations of Cu, Zn, Pb and Fe were recorded in algae from Guaymas Bay. Metal concentrations varied seasonally; the highest Fe, Cu, Zn, Ni and Pb levels were recorded in the cold season in algae from both bays. *S. filamentosa* concentrated more Fe, Ni, Cu, Zn and Pb, while *P. mexicana* and *U. ohnoi* showed higher Mn and Cd. Therefore, *S. filamentosa* proved to be the most suitable indicator of metal concentrations, followed by *P. mexicana* and *U. ohnoi*. The high metal concentrations recorded in algae from San Juan de la Costa, La Paz Bay, are related to mining activities, whereas those in algae from Guaymas Bay are related to canneries, maritime traffic and others.

Introduction

Proper evaluation of natural and anthropogenic contributions of trace metals to surface sediments and seawater is challenging given their intrinsically variable concentrations associated with the fluctuating conditions in coastal environments. The analysis of environmental matrices such as water or sediment provides a picture of the total contaminant load rather than the fraction with direct ecotoxicological relevance. The use of biomonitors eliminates the need for complex studies on the chemical speciation of aquatic contaminants and facilitates the evaluation of biologically available levels of contaminants in aquatic ecosystems or their effects on living organisms (Phillips & Segar, 1986; Huerta-Díaz *et al.*, 2007; Ackali & Kucuksezgin, 2011).

Marine organisms are commonly used as bioindicators of trace metal contamination (Volterra & Conti, 2000; Hernández-Almaraz *et al.*, 2016). Algae and molluscs are among the organisms most used for this purpose (Rainbow, 1995). Macroalgae accumulate trace metals, reaching concentrations that are thousands of times higher than levels in seawater (Rai *et al.*, 1981; Bryan & Langston, 1992). Algae bind only free metal ions, the concentrations of which depend on the nature of the suspended particulate matter; this, in turn, comprises both organic and inorganic complexes (Seeliger & Edwards, 1977; Luoma, 1983; Volterra & Conti, 2000). Marine macroalgae are regarded as suitable indicators due to being widely distributed in aquatic environments, sessile, easy to collect and identify, and for bioaccumulating metals in concentrations that can be several orders of magnitude higher than those in the surrounding seawater (Sánchez-Rodríguez *et al.*, 2001; Conti & Cecchetti, 2003; Khaled *et al.*, 2014; Bonanno *et al.*, 2020).

It has been shown that metal concentrations in macroalgae are proportional to the respective dissolved concentration of each in the surrounding water (Huerta-Díaz *et al.*, 2007). Various macroalgae groups have been shown to be good indicators of environmental conditions. For example, green algae such as *Ulva lactuca* (Linnaeus 1753) have a high affinity for manganese (Mn), iron (Fe), copper (Cu), zinc (Zn) and lead (Pb) (Ryan *et al.*, 2012). The brown macroalgae *Fucus vesiculosus* Linnaeus (Giusti, 2001; Ryan *et al.*, 2012), *Ascophyllum nodosum* (Linnaeus) (Le Jolis) 1863, *Laminaria digitata* (Hudson) J.V. Lamouroux (Stengel *et al.*, 2004), *Lessonia trabeculata* Villouta & Santelices 1986, and

L. nigricens Bory (Contreras *et al.*, 2009; Sáez *et al.*, 2012) have been used to monitor metal contamination as well as temporal and intraspecific fluctuations in metal concentrations in coastal waters. Evans & Edwards (2011) also documented that the brown alga *Macrocystis pyrifera* can be used to measure Cu and Zn concentrations in seawater because tissue concentrations follow those in seawater, although there are interactions between both metals (Cu may inhibit Zn uptake). Perhaps more importantly, once these metals are taken up, tissue concentrations fluctuate temporally and the alga can release them (depuration) when seawater concentrations drop. The red macroalgae *Spyridia filamentosa* Wulfen (Harvey) 1833, *Gelidium floridanum* W.R.Taylor 1943 and *Polysiphonia lanosa* Linnaeus (Tandy) 1931 have also been useful for detecting various trace and heavy metals in the environment (Rodríguez-Castañeda *et al.*, 2006; Ródenas de la Rocha *et al.*, 2009; Ryan *et al.*, 2012; dos Santos *et al.*, 2014; Farias *et al.*, 2018).

In Mexico, coastal lagoons are affected by anthropogenic activities in their associated watersheds, such as industry, mining, aquacultural and agricultural expansion, sewage discharges, dredging, and accelerated population growth; metal contamination gradients and high metal concentrations are usually related to these activities (Marín-Guirao *et al.*, 2008; Vizzini *et al.*, 2013; Hatje *et al.*, 2016; Páez-Osuna *et al.*, 2017). Metal concentrations have been measured in macroalgae from the east coast of the Gulf of California over several years (Páez-Osuna *et al.*, 2000; Jara-Marini *et al.*, 2020), as well as in macroalgae from the west coast of the Baja California peninsula (Shumilin *et al.*, 2000; Sánchez-Rodríguez *et al.*, 2001; Rodríguez-Castañeda *et al.*, 2006; Huerta-Díaz *et al.*, 2007). Most studies analysing metals in algae have been carried out as one-time investigations, using a single sample of algae, and in just one survey into the region (Rodríguez-Castañeda *et al.*, 2006); just a few have monitored different seasons over one year, but using a single species (Rodríguez-Figueroa *et al.*, 2009). Previous studies conducted in Guaymas Bay and La Paz Bay involving organisms such as clams, urchins and fish, as well as sediments, measured Cd, Cu, Pb, Zn, Ni and Mn concentrations. Until the past decade, these metals in macroalgae still maintained levels considered typical of non-polluted sites, despite some of these study sites being known for heavy anthropogenic activities that could potentially release toxic wastes into the environment (Méndez *et al.*, 2002, 2004, 2006; Hernández-Almaráz *et al.*, 2014, 2016; Serviere-Zaragoza *et al.*, 2021).

The present study was conducted in Guaymas Bay and La Paz Bay, located on opposite sides of the Gulf of California, to compare metal concentrations in three macroalgae species and how these relate to the anthropogenic activities in adjacent areas. The three algae species studied belong to the Rhodophyta, Chlorophyta and Ochrophyta and are cosmopolitan, abundant and usually found year-round. Around the globe, seaweeds have been included as key organisms for determining and monitoring the ecological status of coastal ecosystems (Ballesteros *et al.*, 2007; Juanes *et al.*, 2008). For example, the brown algae *Padina gymnospora* (Kützing) Sonder 1871 and *Dictyota bartayresiana* J. V. Lamoroux 1809, and the green algae *Ulva lactuca* and *Enteromorpha intestinalis* (Linnaeus) Nees 1820 were suggested as biomonitors for Cd, Ni, Cr, Cu, Zn and Pb in the Gulf of Kutch (India) (Chakraborty *et al.*, 2014), as well as *Gracilaria conferuoides* for As, Cu, Pb, Cr and Fe in Liusha Bay, South China Sea (Caixue *et al.*, 2010). Pan *et al.* (2018) monitored macroalgae in the East China Sea; in their study, macroalgae were suggested as good quality biomonitors of heavy metals in the environment. The European Water Framework has also included macroalgae as biomonitors (Ballesteros *et al.*, 2007; Juanes *et al.*, 2008).

The objectives of the present study were the following: (1) determine whether *Spyridia filamentosa*, *Padina mexicana* and *Ulva ohnoi* could be good indicators of the presence of metals in two bays of the Gulf of California; (2) identify seasonal variability patterns in metal concentrations in the cosmopolitan macroalgae studied; and (3) determine whether metal concentrations are associated with the main anthropogenic activities at each bay.

Materials and methods

Study area

La Paz Bay, located on the south-western coast of the Gulf of California, is a locality where various anthropogenic activities take place, including aquatic tourism and aquaculture. Although no industries are currently operating in the area, mining activities take place at San Juan de la Costa, in the western coast of the La Paz Bay, related to the extraction of phosphorite from a deposit that has been exploited for nearly 30 years (Rodríguez-Castañeda *et al.*, 2006; Servicio Geológico Mexicano, 2008). Guaymas Bay, on the central eastern coast of the Gulf of California, is an important port with intense industrial activity mainly associated with sardine canneries, particularly in the site known as El Paraje (Méndez *et al.*, 2002; Rodríguez-Castañeda *et al.*, 2006; Osuna-Ramírez *et al.*, 2017). From October to August, local fishmeal plants process 600 000 t year^{-1} of sardine and discharge 20 Mm^3 year^{-1} of wastewater with high organic matter content, fatty acid saturation from fish oils and acidic pH (García-Sifuentes *et al.*, 2009; Osuna-Ramírez *et al.*, 2017).

La Paz Bay (LP)

La Paz Bay is located on the south-western littoral of the Gulf of California, at 24°06′–24°47′N 110°18′–110°45′W. It is the largest bay on the eastern coast of the Baja California peninsula; water exchange between the bay and the Gulf of California occurs through the North Mount (350 m depth) and the San Lorenzo Channel (10 m depth) (Obeso-Nieblas *et al.*, 2004). It comprises an area of ~1200 km^2 and is bordered by the Baja California peninsula and the Espiritu Santo Island complex. It has an elongated shape 90 km long by 30 km wide, with a well-defined channel between 220 and 350 m depth; two sections can be distinguished, a shallow area to the south and a deeper section to the north. Four water masses are present in the bay: Surface Tropical Water, Surface Equatorial Water, Gulf of California Water and Subtropical Subsurface Water (Cervantes-Duarte *et al.*, 2021). The local climate is arid dry (BWh), with annual evaporation (215 mm) exceeding precipitation (180 mm) (Monreal-Gómez *et al.*, 2001). Three distinctive seasons can be recognized – cold, dry and rainy seasons – based on patterns of air temperature (15.2–19.3°C from November to February; 17.4–27.1°C from March to June; and 24.4–30.1°C from July to October) and precipitation (maximum precipitation from July to October: 2.1–102.3 mm month^{-1}) (INEGI, 2010). These data were used to select months representative of each season to conduct the sampling: January (cold season), May (dry season) and October (rainy season) of 2016. Based on a preliminary survey of all shallow areas of the bay, three sampling locations with the conspicuous presence of benthic macroalgae and contrasting characteristics and nutrient concentrations were selected (Table 1). The substrate at San Juan de la Costa (SJC, 24°22′30″N 110°42′00″W) consists of boulders and sandy patches; a major mining company operates at this site extracting phosphorite, which is then transported by sea elsewhere for processing (Mesa-Zavala, 2013). Casa del Marino (CM, 24°10′20.8″N 110°18′33.3″W) is a

https://doi.org/10.1017/S0025315422000182 Published online by Cambridge University Press

Table 1. Main characteristics and mean concentration of dissolved inorganic nitrogen (DIN μM) and phosphate (PO_4), as recorded at the study sites between 2013 and 2016

Bay	Site	Depth (m)	Main anthropogenic activities	DIN	PO_4
La Paz Bay	SJC	0.5–1.5	Phosphorite mining extraction, local fishing	24.4	1.8
	CM	0.5–2.0	Waterfront of La Paz City, local fishing, sewage discharges	5.4	0.8
	TE	0.5–1.5	Recreational beach, local fishing	2.8	0.7
Guaymas Bay	AL	0.5–2.0	Shipping port, copper disposal	3.3	0.6
	PA	0.5–3.0	Sardine industry, industrial wastewater discharge	10.9	1.7
San Carlos Bay	CP	0.5–3.0	Pristine conditions, no human activities	2.9	0.5

SJC, San Juan de la Costa; CM, Casa del Marino; TE, El Tecolote; AL, Almagre Grande; PA, El Paraje; CP, Cerro Pastel.
Mean values of Dissolved Inorganic Nitrogen (DIN. μM) and PO_4 (μM) at each site and season obtained from Chávez-Sánchez *et al.* (2018) and this study.

protected shallow area located at the southern part of the bay, in the waterfront of the city of La Paz (250,000 inhabitants). This site is dredged regularly, usually harbours local fishing boats, and constantly receives sewage from the adjacent city. The sandy bottom is covered by boulders, shells and coral remains (Chávez-Sánchez, 2012). The third site, El Tecolote (TE, 24°20′9″N 110°19′00″W), is located near the San Lorenzo Channel; its southern portion is uninhabited, characterized by a hard-rock platform with sandy patches (Figure 1).

Guaymas Bay (GU)

Guaymas Bay is a coastal lagoon located at 27°51′8″N 110° 49′51″W on the central east coast of the Gulf of California. The lagoon stretches across 33.6 km^2, its depth varies between 5–8.5 m, and connects with the sea through a 1.2 km wide, 8 m deep mouth. The local climate is warm dry, with a mean annual temperature over 22°C and a summer rainy season. Based on its geomorphological characteristics and water exchange with the ocean, GU is classified as a restricted coastal lagoon (Kjerfve & Magill, 1989) permanently connected to the sea. It has three entry channels and a well-defined tidal circulation, being a vertically very-well mixed system (Figure 1). It receives sewage discharges of 63 effluents from the city of Guaymas (150,000 inhabitants) and industrial facilities, including a thermal power plant, a cement factory and shipyards. Additionally, seven fish-processing facilities discharge their wastewater into the bay (Osuna-Ramírez *et al.*, 2017). A pier for loading and unloading hydrocarbons, copper and pesticides is located at the inner bay (Méndez *et al.*, 2002). Table 1 shows the main characteristics and concentrations of dissolved inorganic nitrogen (DIN) and phosphate (PO_4) at GU.

Three sampling locations with the conspicuous presence of benthic macroalgae and contrasting anthropogenic activities were selected at GU. Almagre Grande (AL, 27°54′25.3″N 110° 52′22.9″W) is a site where port operations take place, including copper loading and unloading. El Paraje (PA, 27°52′51.1″N 110°51′22.9″W) holds the Fisheries Industrial Park of the city of Guaymas, including seven fishmeal processing plants that operate during the sardine fishing season (October–August). Cerro Pastel (CP, 27°56′8.5″N 110°59′33.3″W), a small island within San Carlos Bay, is a pristine area of sandy bottom and patches of rocky coral surrounded by oceanic water (Figure 1).

Sample collection

Samples were collected in January, May and October in both La Paz Bay and Guaymas Bay. Three macroalgae species, known to be the most abundant ones in the region, were collected at each site: *Spyridia filamentosa* (Rhodophyta), *Ulva ohnoi* M. Hiraoka & S. Shimada (Hiraoka *et al.*, 2004; Melton *et al.*, 2016) (Chlorophyta) and *Padina mexicana* E.Y. Dawson 1944 (Ochrophyta). In the field, macroalgae samples were collected manually by freediving during low tide on each date (dry, rainy, cold seasons) between 0.5 and 1 m depth. Different algal morphotypes were sorted from the samples, and at least 100 g of each morphotype was collected. This material was rinsed in the field with seawater to remove sediments and epibionts and was transported to the laboratory for analysis. In the laboratory, a portion of each macroalgae sample was fixed with 4% formaldehyde seawater for taxonomic identification using the keys for the region by Norris (2010, 2014); current species names were reviewed in AlgaeBase (Guiry & Guiry, 2021). The identified material was then rinsed with deionized water, oven-dried for 48 h at 60°C to constant weight and stored in labelled sterile plastic bags for further processing.

Metal analyses

Each macroalgae sample was processed in triplicate. An ∼0.5 g sample of dried material was digested in a 3:1 nitric acid:hydrogen peroxide solution (reagent grade, Avantor Performance Material, Central Valley, PA) in a microwave oven (Mars 5X, CEM, Matthews, NC). Concentrations of cadmium, lead, copper, zinc, nickel, manganese and iron in the digested samples were quantified by flame atomic absorption spectrophotometry using an air-acetylene flame (Avanta, GBC Scientific Equipment, Braeside, VIC, Australia) (Méndez *et al.*, 2006; Hernández-Almaraz *et al.*, 2014). The accuracy of the analytical methods was validated as per the International Atomic Energy Agency (Reference Material IAEA-392 – trace, minor and major elements in algae). Recovery percentages were all above 95% (Table 2). Metal concentrations are expressed in $\mu g\, g^{-1}$ dry weight. The detection limits were Cd, 0.01; Pb, 0.017; Zn, 0.07; Mn, 0.04, Ni, 0.03; and Fe, 0.07 ($\mu g\, g^{-1}$).

Bioaccumulation coefficient and enrichment factor

To examine whether macroalgae showed enrichment related to their local environment, for each collection site we calculated the bioaccumulation coefficient in each macroalgae species relative to seawater and the Enrichment Factor (EF) in macroalgae relative to sediments. The bioaccumulation coefficient was calculated as the ratio of macroalgae concentration to the concentration in coastal water (to this end, we used the concentration reported for North Pacific Waters; Nozaky, 1997). The Enrichment Factor is defined as the ratio between the concentration of one contaminant in the indicator organism and the environment (water or sediment) relative to a natural reference value (background level) that had been previously reported for sediments (e.g. Loska *et al.*, 1997; Volterra & Conti, 2000). The application of

https://doi.org/10.1017/S0025315422000182 Published online by Cambridge University Press

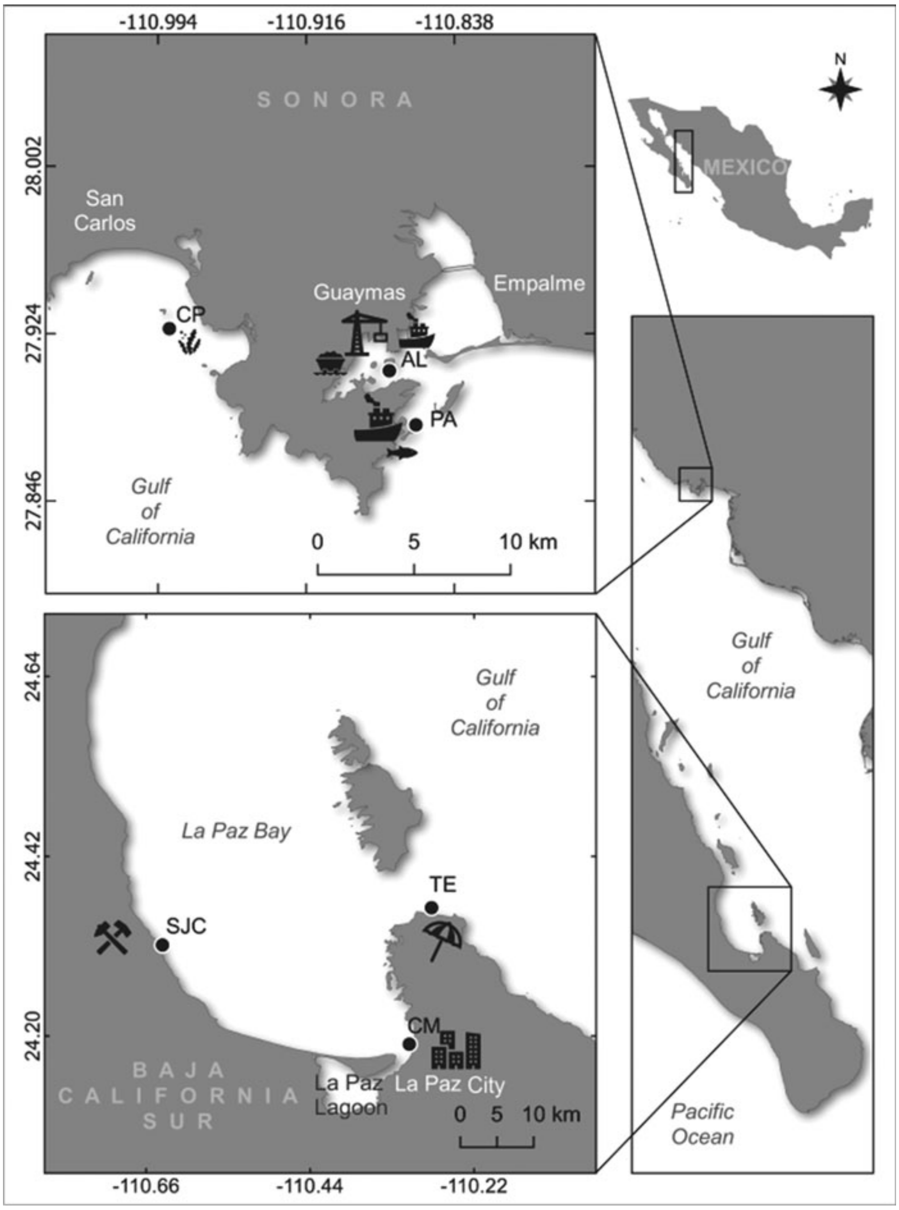

Fig. 1. La Paz Bay and Guaymas Bay. SJC, San Juan de la Costa; CM, Casa del Marino; TE, El Tecolote; AL, Almagre Grande; PA, El Paraje; CP, Cerro Pastel.

Table 2. Analysis of the standard reference material IAEA-392 ($\mu g\ g^{-1}$) (International Atomic Energy Agency, trace, minor and major elements in algae)

Element	Certified	Measured	Recovery (%)
Fe	497 ± 13.6	509 ± 14.2	102
Mn	67.5 ± 1.54	64.9 ± 1.62	96.1
Cu	23.2 ± 1.74	22.7 ± 1.81	97.8
Zn	128 ± 2.0	125 ± 2.5	97.6
Ni	0.571 ± 0.028	0.542 ± 0.031	95.0
Cd	0.0173 ± 0.0014	0.0183 ± 0020	106
Pb	0.574 ± 0.019	0.545 ± 0.028	95.1

EF allowed comparing metal concentrations in macroalgae *vs* marine sediments.

The Enrichment Factor (EF) has been based on the normalization of a tested element against a reference element with low occurrence variability (e.g. Chakraborty *et al.*, 2014). In the study area, the data on the concentrations of metals in water, sediments or algae are insufficient for normalization; thus, we used the element proposed by Pérez-Tribouillier (2014). In La Paz Bay, this author found that Li was the least variable metal, and using it allowed normalizing all other elements in his study. Besides, metal concentrations in sediments were used as a baseline for calculating the Enrichment Factor used in the comparisons.

The Enrichment Factor (EF) was calculated by normalizing the terrigenous element Li, which was the most efficient normalizer (Pérez-Tibouillier *et al.*, 2015), as follows:

$$EF = (M_m/Li_{sediment})/(M_{crust}/Li_{crust})$$

where M_m denotes the concentration of element M (Metal) in macroalgae (m) at each site; Li, the concentration of lithium at each site (in this case, La Paz Bay); M_{crust}, the concentration of element M in the crust, and Li_{crust}, the concentration of lithium in the upper continental crust (Wedepohl, 1995).

Five contamination categories are recognized based on the Enrichment Factor (Buat-Menard & Chesselet, 1979). The values are interpreted as follows: EF < 2, deficiency to mineral enrichment; EF = 2–5, moderate enrichment; EF = 5–20, significant enrichment; EF = 20–40, very high enrichment; EF > 40, extremely high enrichment (Chakraborty *et al.*, 2014).

Table 3. Mean (± std error) metal concentration (μg g^{-1}) by species, site and season of the year (different superscripts denote significant differences)

	Fe	Mn	Cu	Zn	Ni	Cd	Pb
Species							
S. filamentosa	4187.4 ± 435.9^{a}	251.6 ± 53.2	27.6 ± 3.9^{a}	50.2 ± 3.1^{a}	12.6 ± 0.8^{a}	5.0 ± 0.9	15.0 ± 0.9^{a}
P. mexicana	1304.3 ± 205.1^{b}	202.8 ± 44.9	9.3 ± 1.3^{b}	35.8 ± 2.8^{a}	9.1 ± 0.4^{b}	4.8 ± 0.8	11.1 ± 0.8^{ab}
U. ohnoi	946.2 ± 92.8^{b}	76.4 ± 18.8	5.8 ± 0.7^{b}	15.5 ± 0.9^{b}	8.2 ± 0.6^{b}	3.2 ± 0.5	9.9 ± 0.7^{b}
Site							
SJC	3021.2 ± 474.8^{b}	619.1 ± 114.8^{a}	5.0 ± 0.4^{b}	28.9 ± 2.7^{b}	11.7 ± 0.8^{a}	14.0 ± 1.8^{a}	10.1 ± 1.1^{b}
CM	1609.0 ± 213.5^{c}	108.8 ± 12.5^{b}	6.2 ± 0.4^{b}	35.2 ± 3.4^{b}	8.1 ± 0.3^{b}	1.9 ± 0.1^{b}	13.0 ± 0.8^{b}
TE	1503.1 ± 348.2^{c}	104.3 ± 61.1^{b}	3.3 ± 0.3^{b}	15.5 ± 1.9^{c}	9.7 ± 0.8^{b}	4.4 ± 1.3^{c}	14.3 ± 1.0^{a}
AL	5002.3 ± 817.6^{a}	155.1 ± 14.6^{b}	52.6 ± 5.9^{a}	68.3 ± 3.4^{a}	15.2 ± 1.4^{a}	2.1 ± 0.1^{b}	16.2 ± 1.6^{a}
CP	744.2 ± 144.4^{d}	26.8 ± 4.1^{c}	4.9 ± 0.6^{b}	15.1 ± 1.4^{c}	8.3 ± 0.8^{b}	3.2 ± 0.4^{b}	10.7 ± 1.3^{b}
PA	1870.5 ± 357.5^{c}	105.4 ± 57.1^{b}	14.2 ± 2.1^{c}	38.0 ± 4.2^{b}	8.2 ± 0.7^{b}	2.1 ± 0.6^{b}	9.7 ± 0.9^{b}
Season							
Cold	3449.7 ± 444.8^{a}	110.9 ± 21.2	23.5 ± 3.8^{a}	44.0 ± 3.0^{a}	13.1 ± 0.8^{a}	4.0 ± 0.5	16.4 ± 0.7^{a}
Dry	1210.2 ± 161.6^{b}	225.9 ± 61.8	9.6 ± 1.9^{b}	25.3 ± 2.9^{b}	7.8 ± 0.4^{b}	3.7 ± 0.7	9.0 ± 0.8^{b}
Rainy	2028.8 ± 292.6^{ab}	245.6 ± 55.6	10.5 ± 1.3^{b}	33.3 ± 3.2^{ab}	8.6 ± 0.4^{b}	5.7 ± 1.4	9.8 ± 0.8

Statistical analyses

All data were tested for homogeneity and homoscedasticity prior to analysis. MANOVAs, followed by a Tukey's multiple comparison test, as appropriate, were used to explore differences in mean metal concentrations between species, sites, and seasons of the year, separately for each metal (Zar, 2010). Pearson's correlation coefficient was used to assess the correlation between metal concentrations separately for each lagoon. A significance level (α) of 0.05 was used for all tests; all statistical tests were carried out using the software STATISTICA 8 (StatSoft Inc., 2007).

Results

Metal concentrations in algae

Metal concentrations in algae showed significant differences between species, sites and seasons of the year (Table 3). The species *Spyridia filamentosa* showed significantly higher ($P < 0.05$) Fe, Ni and Cu concentrations relative to the other two species examined, as well as higher ($P < 0.05$) Zn and Pb concentrations than *Ulva ohnoi*. However, *Padina mexicana* and *U. ohnoi* showed higher Mn and Cd concentrations ($P < 0.05$; Table 3). There were significant differences between sites ($P < 0.05$). Algae from SJC had significantly higher Mn and Cd concentrations; algae from AL had higher Fe, Cu, Zn and Pb levels; and Ni was higher in algae from SJC and AL (Table 3). As regards seasons, Cu, Ni, Pb and Fe concentrations in algae were significantly higher ($P < 0.05$) during the cold season, while Mn and Cd showed no seasonal differences (Table 3).

Considering the three variables combined (i.e. site, species and season), significant differences in metal concentrations were also evident. The highest Fe concentration was found in *Spyridia filamentosa* from AL and PA in the cold season; Mn concentration was higher in *S. filamentosa* from SJC in the dry and rainy seasons and in *Padina mexicana* in the rainy season (Figure 2A, B). The highest Cu concentration was recorded in *S. filamentosa* from AL in the cold season. The highest concentration of Zn was found in *S. filamentosa* and *P. mexicana* from AL and PA in the three seasons (Figure 2C, D). The highest Ni concentrations were observed in *S. filamentosa* from AL, CP and PA in the cold season and in *Ulva ohnoi* from SJC in the cold season. The highest Cd concentrations were recorded in *S. filamentosa* and *P. mexicana* from SJC in the three seasons. The concentration of Pb was highest in *S. filamentosa* and *U. ohnoi* from AL and CP in the cold season (Figure 2E–G).

Bioaccumulation coefficient and enrichment factor

The bioaccumulation coefficient for each species showed values in excess of 50,000 for Fe, followed by values in the order of thousands for Mn and Pb, between 40–300 for Cu, Zn and Cd, and attained the lowest values for Ni at between 17–26. *Spyridia filamentosa* showed the highest bioaccumulation coefficient for all metals (Figure 3).

In general, the Enrichment Factor attained values within the category Deficiency to Mineral Enrichment (<2) for all metals. The exceptions were Cu in Almagre Grande (Moderate Enrichment, 2–5) and Cd in SJC, with EF values ranging from Very High Enrichment (20–40) to Extremely High Enrichment (>40) (Figure 4).

Correlation between metal concentrations

Significant positive correlations were found between Fe-Mn, Fe-Cu, Fe-Zn, Fe-Ni, Fe-Cd, Fe-Pb, Mn-Ni, Mn-Cd, Cu-Zn and Zn-Pb at La Paz Bay. In contrast, Mn-Pb and Cd-Pb showed significant negative correlations. At Guaymas Bay, significant positive correlations were found between Fe-Mn, Fe-Cu, Fe-Zn, Fe-Ni, Fe-Pb, Mn-Zn, Mn-Cd, Cu-Zn, Cu-Ni, Cu-Pb, Zn-Pb and Ni-Pb (Table 4).

Discussion

Previous studies reported significant differences in metal concentrations between sites and between species; this information is summarized in Table 5. From these studies, authors have found that, in general, brown algae showed the highest metal concentrations, followed by red and green algae (Sánchez-Rodríguez *et al.*, 2001), while in the continental portion of the Gulf of California, green algae showed the highest concentrations (Páez-Osuna *et al.*,

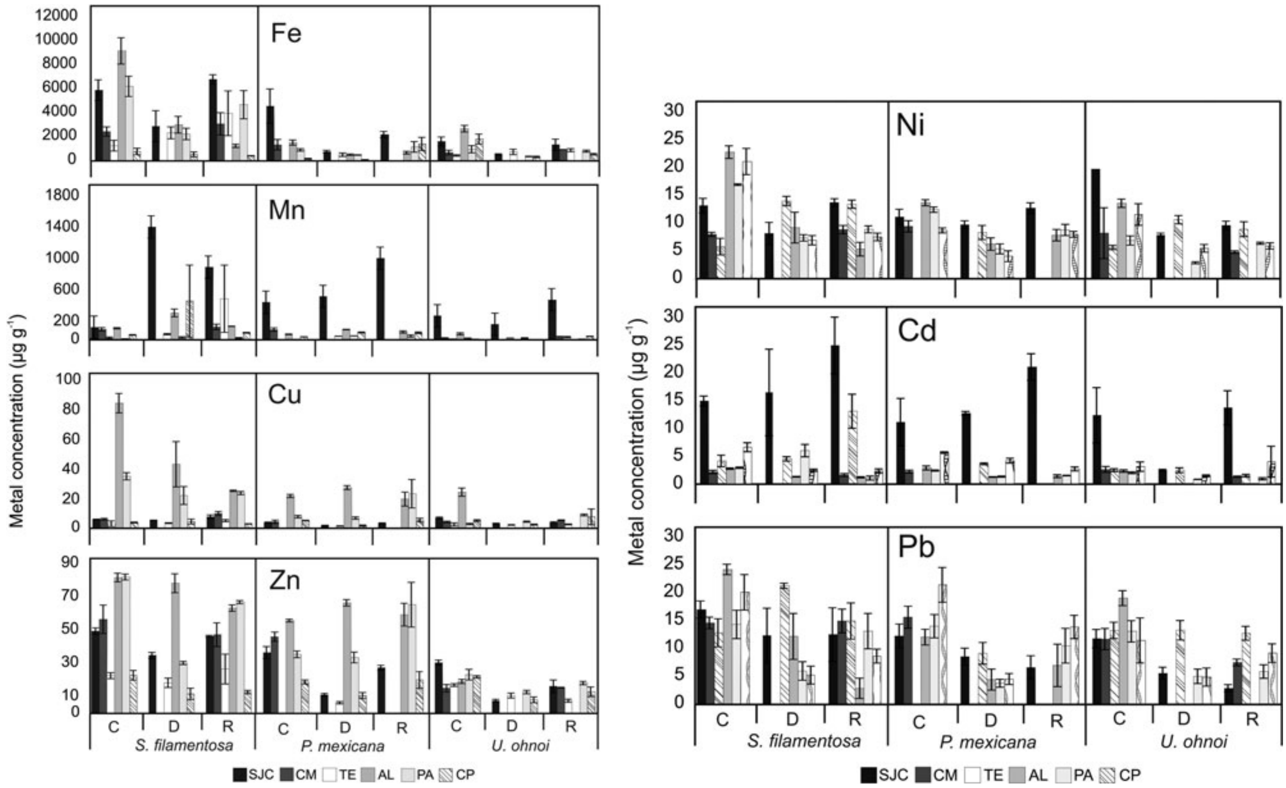

Fig. 2. Mean concentrations (µg g^{-1}) of Fe, Mg, Cu, Zn, Ni, Cd and Pb in tissues of three macroalgae species, *Spyridia filamentosa*, *Padina mexicana* and *Ulva ohnoi* from different sites in three contrasting seasons of the year 2016. SJC, San Juan de la Costa; CM, Casa del Marino; TE, El Tecolote; AL, Almagre; PA, El Paraje; CP, Cerro Pastel; C, cold season; D, dry season; R, rainy season.

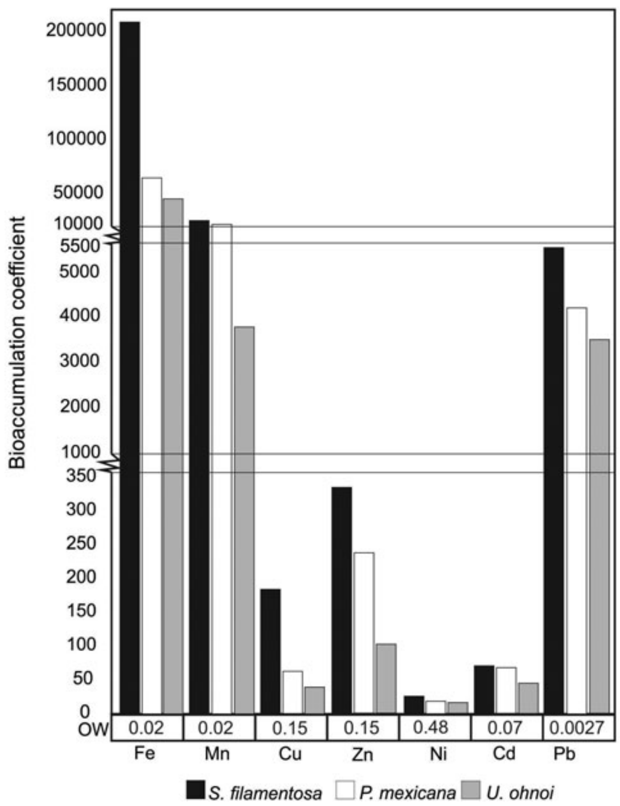

Fig. 3. Bioaccumulation coefficient of each macroalgae species in relation to water concentrations for each metal. OW = Oceanic Water concentrations (µg l^{-1}).

2000). However, other studies have found no significant differences in metal concentrations between macroalgae species or groups (Rodríguez-Castañeda *et al.*, 2006; Huerta-Diaz *et al.*, 2007). These findings suggest that any of the macroalgae species could be used as a good indicator of metal concentrations. Further, longer-term studies examining particular species at different sites or focusing on physiological aspects of some of these species are needed to elucidate why some species accumulate more metals than others under certain conditions, as observed in the present study.

Metal concentrations in seaweed species may reflect their particular morphology, as those with a larger surface area have higher metal contents in tissues. Growth rates can also affect bioaccumulation patterns, with faster-growing specimens showing lower concentrations (Lobban & Harrison, 1994). It has also been found that different seaweed species have distinct affinities for different heavy metals. This may reflect competition between metals for binding or uptake sites in the seaweed (Akcali & Kucuksezgin, 2011). For example, in *U. lactuca*, trace elements can be adsorbed on the surface or stored in the cells within the cytosol (Turner *et al.*, 2008). Metal surface complexation prompts adsorption, whereas internalization can occur as a result of surface complexation or autonomously as a passive process in the case of lipophilic metal complexes (Mason *et al.*, 1996; Bonanno *et al.*, 2020). Brown algae are highly selective for bivalent metals, which they take up from seawater (Volterra & Conti, 2000).

Differences in metal concentrations in algae between sites can be found because of the source of metals and background metal concentrations, such as discharges of household and industrial effluents (Osuna-López *et al.*, 1989; Páez-Osuna *et al.*, 2000) that influence metal bioavailability (Marín-Guirao *et al.*, 2008; Vizzini *et al.*, 2013; Hatje *et al.*, 2016; Páez-Osuna *et al.*, 2017). For example, algae from SJC and AL generally showed the highest metal concentrations (Mn, Cd and Ni in SJC and Fe, Cu, Zn, Pb and Ni in AL); both sites are influenced by anthropogenic activities (one site is located in the vicinity of a mine and the second at the cargo port) and phosphorite mining operations at SJC might

https://doi.org/10.1017/S0025315422000182 Published online by Cambridge University Press

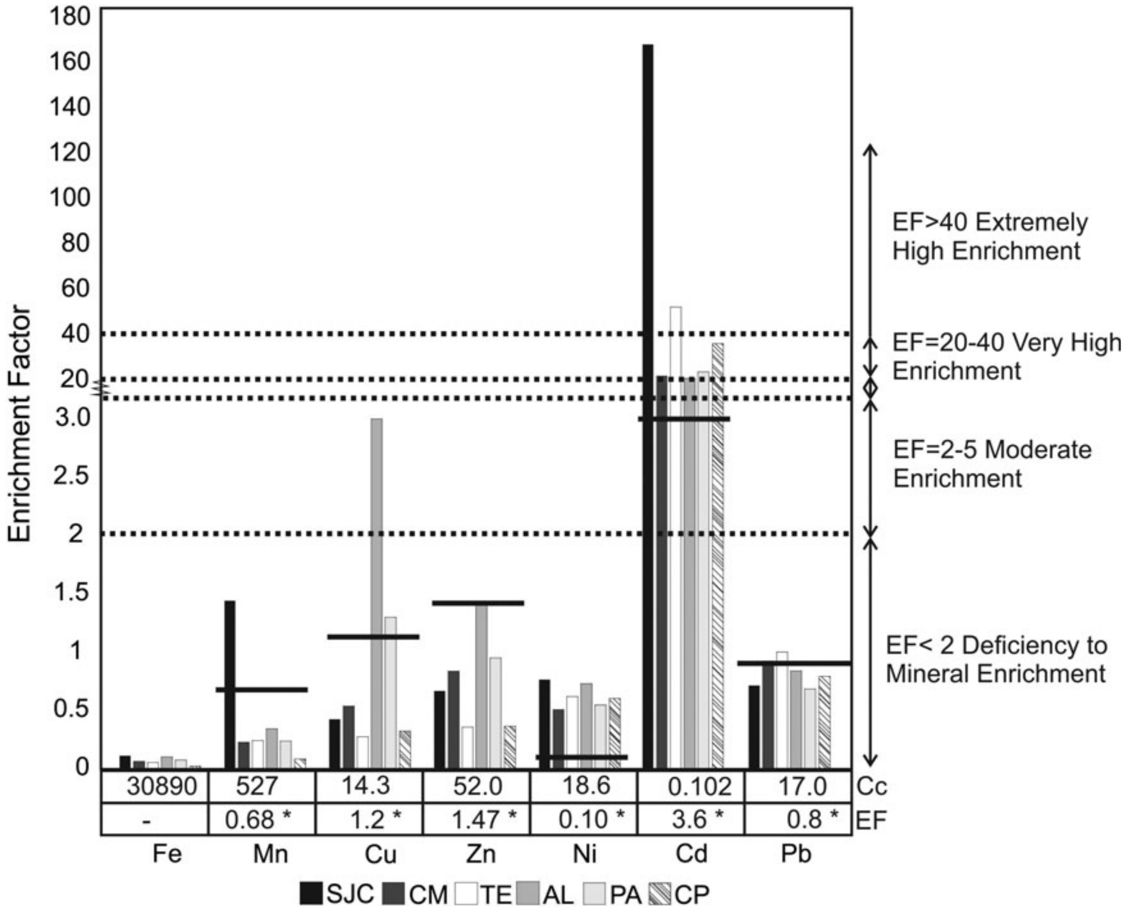

Fig. 4. Enrichment Factor (EF) in macroalgae at each sampling site for each metal, in relation to sediment concentrations. * Sediment EF values from Pérez-Tiboullier (2014). Note that some values were calculated specifically for this study, so they are approximate values. EF could not be calculated for iron. SJC, San Juan de la Costa; CM, Casa del Marino; TE, El Tecolote; AL, Almagre Grande; PA, El Paraje; CP, Cerro Pastel. Cc, sediment metal concentration of the continental crust (μg g^{-1}).

Table 4. Correlations between metal concentrations recorded in algae from La Paz Bay and Guaymas Bay in 2016

		Fe	Mn	Cu	Zn	Ni	Cd	Pb
La Paz Bay	Fe	1	**0.37**	**0.46**	**0.65**	**0.43**	**0.51**	**0.32**
	Mn	**0.37**	1.00	0.07	0.17	**0.33**	**0.85**	**−0.24**
	Cu	**0.46**	0.07	1.00	**0.65**	0.14	0.03	0.23
	Zn	**0.65**	0.17	**0.65**	1.00	0.13	0.19	**0.33**
	Ni	**0.43**	**0.33**	0.14	0.13	1.00	**0.51**	0.21
	Cd	**0.51**	**0.85**	0.03	0.19	**0.51**	1.00	**−0.24**
	Pb	**0.32**	**−0.24**	0.23	**0.33**	0.21	**−0.24**	1.00
Guaymas Bay	Fe	1.00	**0.22**	**0.88**	**0.69**	**0.69**	0.05	**0.59**
	Mn	**0.22**	1.00	0.17	**0.24**	0.07	**0.66**	−0.05
	Cu	**0.88**	0.17	1.00	**0.81**	**0.72**	−0.04	**0.63**
	Zn	**0.69**	**0.24**	**0.81**	1.00	**0.61**	−0.11	**0.47**
	Ni	**0.69**	0.07	**0.72**	**0.61**	1.00	0.19	**0.76**
	Cd	0.05	**0.66**	−0.04	−0.11	0.19	1.00	0.13
	Pb	**0.59**	−0.05	**0.63**	**0.47**	**0.76**	0.13	1.00

Values in bold are significantly different from zero.

increase minerals draining off from the mine to coastal water during the extraction processes (Föllmi *et al*., 2019).

No seasonal monitoring studies have been carried out previously in this region. Some studies have shown that metal concentrations in macroalgae vary with the season of the year (Páez-Osuna & Marmolejo, 1990; Jara-Marini *et al*., 2013*a*, 2013*b*, 2020). High metal concentrations recorded in the spring in several studies have been related to high photosynthetic rates

https://doi.org/10.1017/S0025315422000182 Published online by Cambridge University Press

https://doi.org/10.1017/S0025315422000182 Published online by Cambridge University Press

Table 5. Comparison of metal concentrations (μg g^{-1}) recorded in different macroalgae species from the Pacific Coast and the Gulf of California

Site	Species	Fe	Mn	Cu	Zn	Ni	Cd	Pb	Reference
Gulf of California and Pacific Coast	*Spyridia filamentosa*	1318		7.4	29.2	13.3	3.7	–	Páez-Osuna *et al.* (2000)
	Padina durvillei	487	–	–	36.7	3.5	5.6	–	
	Ulva species	274–4030		4.7-22.6	8.8–99.8	3.7–32.9	2–11.7	–	
Loreto Bay, BCS	Red algae	200–4500	–	–	21–6	40–200	–	–	Sánchez-Rodríguez *et al.* (2001)
	Codium cuneatum	120–350	–	–	8–23	10	–	–	
	Padina durvillei	300–7200	–	–	23–81	30–40	–	–	
La Paz Bay, BCS	*S. filamentosa*	0.1–1.2 (%)	–	–	20–60	–	–	–	Rodríguez-Catañeda *et al.* (2006)
	P. mexicana	0.6–1.6 (%)	–	–	40–50	–	–	–	
	U. tepida (as *U. intestinalis*)	0.7–1.4 (%)	–	–	40–50	–	–	–	
Gulf of California	*Gracilariopsis lameneiformis*	846.0 ± 1472	17 ± 12	2.2 ± 1.0	12.8 ± 7.3	4.26 ± 0.9	–	28.0 ± 14.0	Huerta-Díaz *et al.* (2007)
	Sargassum sinicola	186.0 ± 75	8.1 ± 4.0	3.0 ± 0.7	9.3 ± 9.4	5.1 ± 1.5	–	30.0 ± 19.0	
	Ulva lactuca	1053.0 ± 1389	16.5 ± 9.5	3.3 ± 1.2	8.9 ± 3.1	6.6 ± 2.1	–	16.1 ± 2.1	
Estero de Urías, Sinaloa	*Gracilaria* sp.	–	–	2.95 –8.20	2.96–17.32	–	0.18 –0.29	1.51 –5.38	Jara-Marini *et al.* (2009)
	Ulva sp.	–	–	7.60 ± 3.60	8.49 ± 3.77	–	0.14 ± 0.02	1.89 ± 0.61	
Santa Rosalía, BCS	*P. durvillei*	30–8600	20–860	2.0–115	8–168	4.6–28	1.45–9.1	1.5–30	Rodríguez-Figueroa *et al.* (2009)
El Tobari lagoon, Sonora	*S. filamentosa*	–	–	2.33–3.07	14.35–20.78	–	0.33–0.75	0.86–0.97	Jara-Marini *et al.* (2020)
	Ulva species	–	–	2.18–8.96	10.14–47.44	–	0.35–0.8	0.84–0.96	
La Paz Bay, BCS	*S. filamentosa*	396.54–7706.06	5.99–2189.91	1.44–13.50	10.68–77.16	3.41–14.54	0.86–37.08	7.08–22.24	This study
	P. mexicana	327.40–8619.15	43.65–1505.96	1.63–7.77	4.74–52.79	5.36–13.75	1.47–25.16	2.39–18.34	
	U. ohnoi	151.75–2245.69	5.44–589.22	0.87–8.08	5.84–32.61	4.32–26.65	1.01–19.15	1.77–19.45	
Guaymas Bay, Sonora	*S. filamentosa*	54.82–16705.29	8.77–1866.59	1.39–133.15	4.15–98.12	3.14–30.77	0.55–19.48	0.29–34.56	
	P. mexicana	92.31–3305.61	6.64–135.29	1.70–41.63	8.63–86.59	3.03–14.45	0.97–5.66	1.16–25.28	
	U. ohnoi	155.41–3135.48	4.29–102.40	1.93–29.81	4.42–27.62	2.50–15.14	0.31–9.31	0.46–21.33	

Table 6. Comparison of metal concentrations recorded in different sites influenced by various anthropogenic activities from the Pacific Coast and Gulf of California (sediment or water)

Site	Anthropogenic activities	Matrix	Fe	Mn	Cu	Zn	Ni	Cd	Pb	Reference
North Pacific	None	Water (converted from original to μg l^{-1})	0.02	0.02	0.15	0.15	0.48	0.07	0.0027	Compiled by Nozaki (1997)
Guaymas Basin	Deep-water samples (warm)	Water (μM)	7.5	1.48	0.29	18.75			16	Demina *et al.* (2009)
Gulf of California Estero de Urías, Sinaloa	Industrial zone	Water (μg l^{-1})	–	–	1.75–3.61	0.31–1.79	–	0.25–0.75	1.48–3.64	Jara-Marini *et al.* (2009)
La Paz Lagoon	Drainage area of the La Paz City	Sediments (μg g^{-1})	1.5 ± 0.7	180.0 ± 97						Kot *et al.* (1999)
South-eastern Baja California, Santa Rosalía	Cu mine	Sediments ppm	2.8%	–		192.5	100.3	–	–	Shumilin *et al.* (2000) *approximate values taken from the superficial layer reported by the authors
San Juan de la Costa	Phosphorite mine	Sediments	2.1	–	–	1.6	70	–	–	
Guaymas Bay	Main unload dock for materials such as copper, grains, and various chemical compounds	Sediments (μg g^{-1})	–	177	339.0	135	26.5	1.8	36.3	Méndez *et al.* (2004)
	Municipal wastewater	Sediments (μg g^{-1})	–	153.5	186.5	421	28.5	4.8	14.5	
	Industrial activities	Sediments (μg g^{-1})	–	151	90.8	359	32.3	5.1	56.5	
Estero de Urías, Sinaloa	Industrial zone	Sediments (μg l^{-1})	–	–	16.0–19.4	21.3–35.8	–	0.46–0.69	6.1–10.3	Jara-Marini *et al.* (2009)
La Paz Lagoon, B.C.S.		Sediments	1.97%	296		48.8	1.58	0.3	11.1	Pérez-Tribouillier (2014)
El Soldado lagoon, Sonora	Pristine system	Sediments (μg g^{-1})	1.05 ± 0.24	93.3 ± 22.2	7.5 ± 2.28	32.1 ± 7.03	19.5 ± 3.09	1.76 ± 0.18	10.3 ± 1.55	Vargas-González *et al.* (2017)
Lobos lagoon, Sonora	Receives urban and agriculture wastewater	Sediments (μg g^{-1})	2.76 ± 0.20	316 ± 64.1	16.30 ± 2.26	70.1 ± 6.15	20.5 ± 8.31	1.22 ± 0.22	18.5 ± 2.63	
Tobari lagoon, Sonora	Receives urban, shrimp farming, and agriculture wastewater	Sediments (μg g^{-1})	2.53 ± 0.31	747 ± 99.7	11.3 ± 1.94	51.4 ± 6.08	11.2 ± 1.79	1.12 ± 0.21	16.0 ± 2.08	
El Tobari lagoon, Sonora	Receives urban, shrimp farming, and agriculture wastewater	Sediments (μg g^{-1})			4.37–11.35	10.7–25.77		0.62–0.87	0.73–0.93	Jara-Marini *et al.* (2020)

as macroalgae biomass increases (Strezov & Nonova, 2003). Seasonal differences in algal metabolism explain the variations observed in metal concentrations in algal tissue (Vasconcelos & Leal, 2001).

High Fe concentrations in macroalgae, relative to other heavy metals, are associated with the role of this metal in organisms and high photosynthesis rates in tropical coastal habitats (Chakraborty *et al.*, 2014). The high Fe concentrations recorded (2000 and 13,000 $\mu g\,g^{-1}$) in the macroalgae studied were far above those recorded in other studies in the same region. Concentrations between 2000–7200 $\mu g\,g^{-1}$ have been reported in the region (Páez-Osuna *et al.*, 2000; Sánchez-Rodríguez *et al.*, 2001; Table 5). However, Fe accumulation by macroalgae could be up to three orders of magnitude higher when they grow in polluted environments (Gosavi *et al.*, 2004); this might be the case in AL and PA, particularly during the cold season, when these sites are exposed to more activity from the fishing season and increased port activities (Table 1). Other studies have related high Fe concentrations in macroalgae to industrial activities, as most macroalgae species bioaccumulate Fe from the surrounding environment (Storelli *et al.*, 2001).

As Mn participates in macroalgae metabolism, it is likely to be found at higher tissue concentrations relative to other metals (Strezov & Nonova, 2003). Similar to Fe, Mn values recorded in the present study were higher than those previously reported in the literature (Table 5). Such high Mn concentrations, particularly in SJC, may be related to the mining operations, regardless of the season. Rodríguez-Figueroa *et al.* (2009) found Mn concentrations of 20–860 $\mu g\,g^{-1}$ in macroalgae from Santa Rosalía, which were related to mining extraction operations (Table 5). The correlations between the concentration of Fe, Mn, Cu and Zn at La Paz Bay and between Fe, Mn, Cu, Zn and Ni at Guaymas Bay suggest that all these metals come from common sources.

In Guaymas Bay, as already mentioned, there are inputs of various pollutants, particularly at AL from port operations such as loading and unloading of substances and materials, that cause spills of fuels, pesticides and additives with high contents of heavy metals such as Cu, Pb, Ni and Mn, in addition to the incidental release of copper (Méndez *et al.*, 2006). At this site, Cu concentrations in macroalgae reached peak levels. Cu levels ranging from 200–300 $\mu g\,g^{-1}$ have been recorded in species from polluted areas (Hawk *et al.*, 1974). However, this was the case only for AL since Cu concentrations at the other sites were lower than levels indicating polluted areas. Cu concentrations in macroalgae collected in other shipping ports have also been related to oil pollution and airborne pollutants released by commercial vessels (Chakraborty *et al.*, 2014). Biggs & D'Anna (2012) found that Cu concentrations in water increased soon after boats were introduced into marinas, as the primary sources of Cu were leachates from Cu-based paints from boats. Today, more than 1000 different types of boats and vessels arrive at Guaymas Bay (Méndez *et al.*, 2002).

According to Lobban & Harrison (1994), enzyme cofactors may regulate the concentration of Mn, Cu, Zn and Ni, whereas activators of dehydrogenases and enzymes involved in protein synthesis may also regulate Zn concentration. Elements such as Fe, Cu, Mn, Zn and Co (in vitamin B12) may accumulate in algal tissue as they are important nutrients (Huerta-Díaz *et al.*, 2007). However, environmental concentrations are also important for determining the source of metals.

Nickel is an element associated with oil refining and combustion and marine traffic (Brito *et al.*, 2016). We recorded Ni concentrations higher than those reported elsewhere, suggesting Ni contamination in our study areas, particularly at SJC, AL and PA. Similarly high Ni concentrations have been recorded in the marine seagrass *Halodule wrightii* Ascherson 1868 (9.56 $\mu g\,g^{-1}$) from a site near the shipping routes of Todos os Santos Bay, Brazil (Brito *et al.*, 2016), suggesting that algae growing in sites near shipping routes may show high Ni concentrations.

In benthic macrophytes in general, Zn levels below 100 $\mu g\,g^{-1}$ are suggested as a benchmark for non-polluted areas (Moore & Ramamurti, 1987). Say *et al.* (1990) proposed three concentration ranges (dry weight) of Zn in *Ulva* (as *Enteromorpha*) as an indication of the degree of pollution in estuaries: 50 $\mu g\,g^{-1}$ for non-polluted areas, 50–150 $\mu g\,g^{-1}$ for moderately polluted areas and 150 $\mu g\,g^{-1}$ for heavily polluted areas. In our study, Zn concentrations in *Ulva* were all below 50 $\mu g\,g^{-1}$; however, since we recorded higher values in *Spyridia filamentosa* (up to 73 $\mu g\,g^{-1}$), we can assume that this indicates moderately polluted conditions, particularly at AL and PA. In the Gulf of Kutch in India, sources of Zn have been associated with effluents from the cement industry and a thermal power plant, as shown by the various algae species sampled (Chakraborty *et al.*, 2014). In the surroundings of AL there is also an operating cement plant which can influence high Zn concentrations at this site. In contrast, the low Zn concentrations found at El Tecolote and Cerro Pastel indicate little or no influence from human activities. This is consistent with the results from a study on four macroalgae species from the Strait of Magellan, Chile, where Zn concentration was 41.76 $\mu g\,g^{-1}$, well within the range considered indicative of unpolluted water (Astorga-España *et al.*, 2008).

Cadmium and Pb are toxic heavy metals that pose a global environmental issue. These heavy metals are non-essential, non-biodegradable and are bioaccumulated by absorption or uptake (Sarada *et al.*, 2014). Like the other metals, high Cd concentrations were found at San Juan de la Costa. In addition to mining, in this zone phosphate rocks are also primary sources of Pb, As, Cd and Zn (Nziguheba & Smolders, 2008). Cadmium concentrations in algae suggest an evident variation in uptake levels across sites, showing that bioaccumulation largely depends on environmental pollution levels (Hashim & Chu, 2004; Chakraborty *et al.*, 2014).

Although Pb was found in tissue from macroalgae collected in our study sites, Pb concentrations were within the range of the average abundance in the Earth's crust (3–30 $\mu g\,g^{-1}$) (Smith *et al.*, 1996; Soto-Jiménez *et al.*, 2006). Burdon-Jones *et al.* (1975) and Agadi *et al.* (1978) reported that Pb levels greater than 100 $\mu g\,g^{-1}$ (dry weight) are related to contaminated water (Storelli *et al.*, 2001; Akcali & Kucuksezgin, 2011). However, the Pb concentrations recorded in the present study were below this limit; therefore, our study sites can be considered non-polluted by Pb. As for the other metals quantified, the levels in macroalgae associated with seawater pollution are yet to be determined.

In the Gulf of California, metal concentrations in the water column have been determined, but data are still scarce; some of the available data are summarized in Table 6. According to these data, oceanic water levels in the North Pacific are low, while seawater concentrations in samples from areas with anthropogenic activities are higher. The values recorded in macroalgae in our study are several orders of magnitude higher than the values reported in seawater, consistent with previous literature reports suggesting that macroalgae bioaccumulate metals present in the surrounding water.

Metal concentrations in sediments obtained for locations resembling our sampling sites were similar to the levels recorded in macroalgae (Table 6), also indicating the relationship with a pristine site or a site with anthropogenic activity, as discussed above. Metal concentrations in macroalgae vary greatly between sites and between seasons, and there are also insufficient data on metal concentrations in seawater and sediments for the study area. Consequently, it was impossible to conclude whether macroalgae are effectively bioaccumulating elements or are suitable bioindicators of environmental conditions. For this reason, we used the Enrichment Factor, which has been used for sediments and describes a range of environmental conditions, from mild to heavily polluted by metals (Loska *et al*., 1997; Kaushik *et al*., 2009). Enrichment Factor values for Mn, Zn and Pb in macroalgae were lower than in sediments, except for Mn at SJC and Pb at ET. In contrast, Cu levels were higher at Almagre Grande and El Paraje, while Ni and Cd showed high concentrations in all sites. This suggests that macroalgae are suitable indicators of both metals and anthropogenic activities, as the high values observed in each site were consistent with anthropogenic activities. These findings agree with the observations reported by Pérez-Tribouillier (2014) for La Paz Bay, where conditions ranged from unpolluted to low mineral levels. Chakraborty *et al*. (2014) found different enrichment values for several metals in sediments, depending on the anthropogenic activities in the vicinity of the sites studied. In the present study, metal concentrations in macroalgae were higher than metals concentrations in seawater in all cases (Figure 3) and, occasionally, metal concentrations in algae exceeded those in sediments, except for sites on the coast of Sonora subjected to higher impacts from anthropogenic activities (Table 6). In a study by Pan *et al*. (2018), the bioaccumulation coefficient for metals in macroalgae was tens- to thousands-fold higher relative to metal levels in seawater, which is consistent with the observations in the present study. These findings support the conclusion that the Enrichment Factor and the bioaccumulation coefficient estimated in macroalgae are good indicators of metal concentrations in the environment where macroalgae thrive.

Our findings suggest that the macroalgae species examined might be suitable indicators of marine contamination since they are easy to collect and provide detailed information on metals in their local environment. Of the species studied, *Spyridia filamentosa* could be the best indicator for Fe, Ni, Cu, Zn and Pb, and *P. mexicana* and *U. ohnoi* for Mn and Cd concentrations. In this ranking order, any of the three species can be used as an indicator of metal concentrations. These species may be sampled year-round in most coastal regions during low tide; sorting macroalgae samples into species is strongly recommended, assisted with particular keys according to the region (e.g. Norris, 2010, 2014) or using the tool AlgaeBase (Guiry & Guiry, 2021). This approach would allow any investigator or environmental manager to collect macroalgae species to monitor environmental metal concentrations, and is also cost-effective since macroalgae can be collected from the shore in some regions. Monitoring activities in coastal regions are relevant given the growing human populations in these areas, leading to increased anthropogenic pressure on marine environments.

Conclusions

Spyridia filamentosa concentrated the largest amounts of metals and is therefore regarded as the best indicator, followed by *P. mexicana* and *U. ohnoi*. Our findings indicate that the three species studied are suitable for monitoring metal concentrations in marine environments. The bioaccumulation coefficient and the Enrichment Factor showed that macroalgae are suitable indicators of seawater quality and metal concentrations in the surrounding environment. Metal concentrations in the three macroalgae species studied varied between sites according to environmental pollution derived from anthropogenic activities during the cold season. The site with the highest Cd and Mn concentrations was San Juan de la Costa (SJC); the highest Fe, Zn, Cu, Pb and Ni concentrations were recorded in algae collected from Almagre Grande (AL). The high metal concentrations in macroalgae from SJC are related to mining activities, while those found at AL are related to industrial activities such as canneries and maritime traffic, among others. Metal concentrations in macroalgae indicate that environmental concentrations are highly variable in both bays. This was expected since anthropogenic activities, including maritime traffic, sardine fishing, industrial activities (especially canneries), mining, and port operations, are also highly variable in terms of quantity, intensity and season when such activities take place.

Acknowledgements. We thank Efrain López Montaño and Edgar Alcántara for their assistance in the field with sample collection and Baudilio Acosta Vargas and Griselda Peña Armenta for analytical work. We also thank Mr Refugio López Tapia from the Laboratorio de Química of CIBNOR for his technical assistance. This study was funded by Consejo Nacional de Ciencia y Tecnología (funder Id: http:/dx.doi.org/10.13039/501100003141) through research grant CONACYT-CB154415, by CIBNOR through grant PC 0.5, and by SEP-CONACyT through grant A1-S-26700. Piñón-Gimate, Cervantes-Duarte and Casas-Valdez thank the Instituto Politécnico Nacional (funder Id: http:/dx.doi.org/10.13039/501100003069) for Estímulo al Desempeño a la Investigación (EDI) and Comisión de Fomento a las Actividades Académicas (COFAA) scholarships. María Elena Sánchez-Salazar edited the English version of the manuscript.

References

Agadi VV, Bhosle NB and Untawale AG (1978) Metal concentration in some seaweeds of Goa (India). *Botanica Marina* **21**, 247–250.

Akcali I and Kucuksezgin F (2011) A biomonitoring study: heavy metals in macroalgae from eastern Aegean coastal areas. *Marine Pollution Bulletin* **62**, 637–645.

Astorga-España MS, Calisto-Ulloa NC and Guerrero S (2008) Baseline concentrations of trace metals in macroalgae from the Strait of Magellan, Chile. *Bulletin of Environmental Contamination and Toxicology* **80**, 97–101.

Ballesteros E, Torras-Bouldú X, Pinedo S, García M, Mangialajo M and de Torres M (2007) A new methodology based on littoral community cartography for the implementation of the European water framework directive. *Marine Pollution Bulletin* **55**, 172–180.

Biggs TW and D'Anna H (2012) Rapid increase in copper concentrations in a new marina, San Diego Bay. *Marine Pollution Bulletin* **64**, 627–635.

Bonanno G, Veneziano V and Piccione V (2020) The alga *Ulva lactuca* (Ulvaceae, Chlorophyta) as a bioindicator of trace element contamination along the coast of Sicily, Italy. *Science of the Total Environment* **699**, 134329.

Brito GB, de Souza TL, Costa FDN, Moura CW and Korn MGA (2016) Baseline trace elements in the seagrass *Halodule wrightii* Aschers (Cymodoceaceae) from Todos os Santos Bay, Bahia, Brazil. *Marine Pollution Bulletin* **104**, 335–342.

Bryan GW and Langston WJ (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution* **76**, 89–131.

Buat-Menard P and Chesselet R (1979) Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth and Planetary Science Letters* **42**, 399–411.

Burdon-Jones C, Denton GRW, Jones GB and McPhic KA (1975) *Metal in Marine Organisms: Part I. Baseline Survey*. Progress Report to the Water Qual. Queensland 4000, Council, Dept. Local Govt., 105 pp.

Caixue Z, Fujin B, Xingli S and Chun-Liang C (2010) Trace elements of spring and winter macroalgae in Liusha Bay. *Oceanologia et Limnologia Sinica* **41**, 154–160.

Cervantes-Duarte R, González-Rodríguez E, Funes-Rodríguez R, Ramos-Rodríguez A, Torres-Hernández MY and Aguirre-Bahena F (2021) Variability of net primary productivity and associated biophysical drivers in Bahía de La Paz (Mexico). *Remote Sensing* **13**, 1644.

Chakraborty S, Bhattacharya T, Singh G and Maity JP (2014) Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: a biomonitoring approach for pollution assessment. *Ecotoxicology and Environmental Safety* **100**, 61–68.

Chávez-Sánchez T (2012) *Composición y abundancia de especies de florecimientos macroalgales y su relación con variables ambientales en la Ensenada de La Paz, Baja California Sur*. Master's thesis, Centro de Investigaciones Biológicas del Noroeste, Baja California Sur, Mexico.

Chávez-Sánchez T, Piñón-Gimate A, Serviere-Zaragoza E, López-Bautista JM and Casas-Valdez M (2018) *Ulva* blooms in the southwestern Gulf of California: reproduction and biomass. *Estuaries Coastal and Shelf Science* **200**, 202–211.

Conti ME and Cecchetti G (2003) A biomonitoring study: trace metals in algae and molluscs from Tyrrhenian coastal areas. *Environmental Research* **93**, 99–112.

Contreras L, Mella D, Moenne A and Correa JA (2009) Differential responses to copper induced oxidative stress in the marine macroalgae *Lessonia nigrescens* and *Scytosiphon lomentaria* (Phaeophyceae). *Aquatic Toxicology* **94**, 94–102.

Demina LL, Galkin SV and Shumilin E (2009) Bioaccumulation of some trace elements in the biota of hydrothermal fields of the Guaymas Basin (Gulf of California). *Boletín de la Sociedad Geológica Mexicana* **61**, 31–45.

dos Santos RW, Schmidt EC, de LFMR, Polo LK, Kreusch M, Pereira DT, Costa GB, Simioni C, Chow F, Ramlov F, Maraschin M and Bouzon ZL (2014) Bioabsorption of cadmium, copper and lead by the red macroalga *Gelidium floridanum*: physiological responses and ultrastructure features. *Ecotoxicology and Environmental Safety* **105**, 80–89.

Evans LK and Edwards MS (2011) Bioaccumulation of copper and zinc by the giant kelp Macrocystis pyrifera. *Algae* **26**, 265–275.

Farias DR, Hurd CL, Eriksen RS and Macleod CK (2018) Macrophytes as bioindicators of heavy metal pollution in estuarine and coastal environments. *Marine Pollution Bulletin* **128**, 175–184.

Föllmi KB, Schöllhorn I, Ulianov A, Adatte T, Spangenberg JE, de Kaenel E and Garrison RE (2019) Phosphogenesis during the Cenozoic transition from greenhouse to icehouse conditions: upper Oligocene to lower Miocene siliceous, phosphate, and organic rich sediments near La Purísima, Baja California Sur, Mexico. *The Depositional Record* **5**, 23–52.

García-Sifuentes C, Pacheco-Aguilar R, Valdez-Hurtado S, Márquez-Ríos E, Lugo-Sánchez M and Ezquerra-Brauer J (2009) Impact of stickwater produced by the fishery industry; treatment and uses. *Journal of Food* **7**, 67–77.

Giusti L (2001) Heavy metal contamination of brown seaweed and sediments from the UK coastline between the Wear River and the Tees River. *Environment International* **26**, 275–286.

Gosavi K, Sammut J, Gifford S and Jankowski J (2004) Macroalgal biomonitors of trace metal contamination in acid sulfate soil aquaculture ponds. *Science of the Total Environment* **324**, 25–39.

Guiry MD and Guiry GM (2021) AlgaeBase. World-wide electronic publication, National University of Ireland, Galway. Available at https://www.algaebase.org (Accessed online 07 July 2021).

Hashim MA and Chu KH (2004) Biosorption of cadmium by brown, green and red seaweeds. *Chemical Engineering Journal* **97**, 249–255.

Hatje V, de Souza MM, Ribeiro LF, Eça GF and Barros F (2016) Detection of environmental impacts of shrimp farming through multiple lines of evidence. *Environmental Pollution* **219**, 672–684.

Hawk A, Melsom S and Omang S (1974) Estimation of heavy metal pollution in two Norwegian fjord areas by analysis of the brown alga *Ascophyllum nodosum*. *Environmental Pollution* **7**, 179–192.

Hernández-Almaraz P, Méndez-Rodríguez L, Zenteno-Savin T, O'Hara TM, Harley JR and Serviere-Zaragoza E (2016) Concentrations of trace elements in sea urchins and macroalgae commonly present in *Sargassum* beds: implications for trophic transfer. *Ecological Research* **31**, 785–798.

Hernández-Almaraz P, Méndez-Rodríguez L, Zenteno-Savín T, García-Domínguez F, Vázquez-Botello A and Serviere-Zaragoza E (2014) Metal mobility and bioaccumulation differences at lower trophic levels in marine ecosystems dominated by *Sargassum* species. *Journal of the Marine Biological Association of the United Kingdom* **94**, 435–442.

Hiraoka M, Shimada S, Uenosono M and Masuda M (2004) A new green-tide-forming alga, *Ulva ohnoi* Hiraoka and Shimada sp. nov. (Ulvales, Ulvophyceae) from Japan. *Phycological Research* **52**, 17–29.

Huerta-Díaz M, De León-Chavira F, Lares MA, Chee-Barragán A and Siqueiros-Valencia A (2007) Iron, manganese and trace metal concentrations in seaweeds from central west coast of the Gulf of California. *Applied Geochemistry* **22**, 1380–1392.

Instituto Nacional de Estadística y Geografía-INEGI (México) (2010) Anuario Estadístico de Baja California. Instituto Nacional de Estadística y Geografía, Gobierno del Estado de Baja California Sur, México. 62 pp.

Jara-Marini ME, Molina-García A, Martínez-Durazo A and Páez-Osuna F (2020) Trace metal trophic transference and biomagnification in a semiarid coastal lagoon impacted by agriculture and shrimp aquaculture. *Environmental Science and Pollution Research* **27**, 5323–5336.

Jara-Marini ME, Soto-Jiménez MF and Páez-Osuna F (2009) Trophic relationships and transference of cadmium, copper, lead and zinc in a subtropical coastal lagoon food web from SE Gulf of California. *Chemosphere* **77**, 1366–1373.

Jara-Marini ME, Tapia-Alcaraz JN, Dumer-Gutiérrez JA, García-Rico L, García-Hernández J and Páez-Osuna F (2013*a*) Comparative bioaccumulation of trace metals using six filter feeder organisms in a coastal lagoon ecosystem (of the central-east Gulf of California). *Environmental Monitoring and Assessment* **185**, 1071–1085.

Jara-Marini ME, Tapia-Alcaraz JN, Dumer-Gutiérrez JA, García-Rico L, García-Hernández J and Páez-Osuna F (2013*b*) Distribution and accumulation of Cd, Cu, Hg, Pb and Zn in the surface sediments of El Tóbari lagoon, central-east Gulf of California: an ecosystem associated with agriculture and aquaculture activities. *Journal of Environmental Science and Health Part A* **48**, 1842–1851.

Juanes JA, Guinda X, Puente A and Revilla JA (2008) Macroalgae, a suitable indicator of the ecological status of coastal rocky communities in the NE Atlantic. *Ecological Indicators* **8**, 351–359.

Kaushik G, Satya S and Naik SN (2009) Food processing: a tool to pesticide residue dissipation – a review. *Food Research International* **42**, 26–40.

Khaled A, Hessein A, Abdel-Halim AM and Morsy FM (2014) Distribution of heavy metals in seaweeds collected along Marsa-Matrouh beaches, Egyptian Mediterranean Sea. *Egyptian Journal of Aquatic Research* **40**, 363–371.

Kjerfve B and Magill KE (1989) Geographic and hydrodynamic characteristics of shallow coastal lagoons. *Marine Geology* **88**, 187–199.

Kot FS, Green-Ruiz C, Páez-Osuna F, Shumillin E and Rodríguez-Meza D (1999) Distribution of mercury in sediments from La Paz lagoon, Peninsula of Baja California, México. *Bulletin of Environmental Contamination and Toxicology* **63**, 45–51.

Lobban CS and Harrison PJ (1994) *Seaweed Ecology and Physiology*. Cambridge: Cambridge University Press.

Loska K, Cebula J, Pelczar J, Wiechuła D and Kwapuliński J (1997) Use of enrichment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik water reservoir in Poland. *Water, Air, and Soil Pollution* **93**, 347–365.

Luoma SN (1983) Bioavailability of trace metals to aquatic organisms – a review. *Science of the Total Environment* **28**, 1–22.

Marín-Guirao L, Lloret J and Marin A (2008) Carbon and nitrogen stable isotopes and metal concentration in food webs from a mining impacted coastal lagoon. *Science of the Total Environment* **393**, 118–130.

Mason RP, Reinfelder JR and Morel FMM (1996) Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environmental Science Technology* **30**, 1835–1845.

Melton JT, Collado-Vides L and López-Bautista JM (2016) Molecular identification and nutrient analysis of the green tide species *Ulva ohnoi* Hiraoka & Shimada 2004 (Ulvophyceae, Chlorophyta), a new report and likely nonnative species in the Gulf of Mexico and Atlantic Florida, USA. *Aquatic Invasions* **11**, 225–237.

Méndez L, Acosta B, Arreola-Lizárraga A and Padilla G (2004) Anomalous levels of heavy metals in sediments from Guaymas Bay, Mexico. *Bulletin of Environmental Contamination and Toxicology* **72**, 1101–1106.

Méndez L, Palacios E, Acosta B, Monsalvo-Spencer P and Álvarez-Castañeda T (2006) Heavy metals in the clam *Megapitaria squalida* collected from wild and phosphorite mine-impacted sites in Baja California, Mexico. *Biological Trace Element Research* **110**, 275–287.

Méndez L, Salas-Flores LM, Arreola-Lizarraga A, Alvarez-Castañeda ST and Acosta B (2002) Heavy metals in clams from Guaymas Bay, Mexico. *Bulletin of Environmental Contamination and Toxicology* **68**, 217–223.

Mesa-Zavala E (2013) *Diagnóstico del hábitat del borrego cimarrón (Ovis canadensis Weemsi) en función de variables ambientales y actividades antropogénicas en la sierra el Mechudo, Baja California Sur, México*. PhD Thesis, Centro de Investigaciones Biológicas del Noroeste, S.C, Baja California Sur, México.

Monreal-Gómez MA, Molina-Cruz A and Salas-de León DA (2001) Water masses and cyclonic circulation in Bay of La Paz, Gulf of California, during June 1988. *Journal of Marine Systems* **30**, 305–331.

Moore JV and Ramamurti S (1987) *Heavy Metals in Near Bottom Water*. Moscow: Mir Publishers, p. 285.

Norris JN (2010) Marine algae of the Northern Gulf of California: Chlorophyta and Phaeophyceae. *Smithsonian Contributions to Botany* **94**, 1–276.

Norris JN (2014) Marine algae of the Northern Gulf of California II: Rhodophyta. *Smithsonian Contributions to Botany* **96**, 1–555.

Nozaki Y (1997) A fresh look at element distribution in the North Pacific. *American Geophysical Union* **78**. 221. http://earth.agu.org/eos_elec97025e.htm

Nziguheba G and Smolders E (2008) Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. *Science of the Total Environment* **390**, 53–57.

Obeso-Nieblas M, Shirasago B, Sánchez-Velasco L and Gaviño-Rodríguez JH (2004) Hydrographic variability in Bahia de La Paz, BCS, Mexico, during the 1997–1998 El Niño. *Deep Sea Research Part II: Topical Studies in Oceanography* **51**, 689–710.

Osuna-López JI, Páez-Osuna F, Marmolejo-Rivas C and Ortega-Romero P (1989) Metales pesados disueltos y particulados en el puerto de mazatlán. *Anales del Instituto de Ciencias del Mar y Limnología UNAM México* **16**, 307–320.

Osuna-Ramírez R, Arreola JA, Padilla-Arredondo G, Mendoza-Salgado RA and Méndez-Rodríguez LC (2017) Toxicity of wastewater from fishmeal production and their influence on coastal waters. *Fresenius Environmental Bulletin* **26**, 6408–6412.

Páez-Osuna F, Álvarez-Borrego S, Ruiz-Fernández AC, García-Hernández J, Jara-Marini ME, Bergés-Tiznado ME, Piñón-Gimate A, Alonso-Rodríguez R, Soto-Jiménez MF, Frías-Espericueta MG, Ruelas-Inzunza JR, Green-Ruiz CR, Osuna-Martínez CC and Sánchez-Cabeza JA (2017) Environmental status of the Gulf of California: a pollution review. *Earth-Science Reviews* **166**, 181–205.

Páez-Osuna F and Marmolejo-Rivas C (1990) Occurrence and seasonal variation of heavy metals in the oyster *Saccrostrea iridescens*. *Bulletin of Environmental Contamination and Toxicology* **44**, 129–134.

Páez-Osuna F, Ochoa-Izaguirre MJ, Bojórquez-Leyva H and Michel-Reynoso IL (2000) Macroalgae as biomonitors of heavy metal availability in coastal lagoons from the subtropical Pacific of Mexico. *Bulletin of Environmental Contamination and Toxicology* **64**, 846–851.

Pan Y, Wernberg T, de Bettignies T, Holmer M, Li K, Wu J, Lin F, Yu Y, Xu J, Zhou C, Huang Z and Xiao X (2018) Screening of seaweeds in the east China Sea as potential bio-monitors of heavy metals. *Environmental Science and Pollution Research* **25**, 16640–16651.

Pérez-Tribouillier H, Shumilin E and Rodríguez-Figueroa GM (2015) Trace elements in the marine sediments of the La Paz lagoon, Baja California Peninsula, Mexico: pollution status in 2013. *Bulletin of Environmental Contamination and Toxicology* **95**, 61–66.

Pérez Tribouillier HU (2014) *Niveles actuales e historia de acumulación de elementos de origen natural y antropogénico en los sedimentos de la Laguna de La Paz, Baja California Sur, México*. M.S. Thesis, Centro Interdisciplinario de Ciencias Marinas. Instituto Politécnico Nacional, La Paz, Baja California Sur, México. [In Spanish].

Phillips DJ and Segar DA (1986) Use of bio-indicators in monitoring conservative contaminants: programme design imperatives. *Marine Pollution Bulletin* **17**, 10–17.

Rai LC, Gaur JP and Kumar HD (1981) Phycology and heavy-metal pollution. *Biological Reviews* **56**, 99–151.

Rainbow PS (1995) Biomonitoring of heavy metal availability in the marine environment. *Marine Pollution Bulletin* **31**, 183–192.

Ródenas de la Rocha S, Sánchez-Muniz FJ, Gómez-Juaristi M and Marín-Larrea MT (2009) Trace elements determination in edible seaweeds by an optimized and validated ICP-MS method. *Journal of Food Composition and Analysis* **22**, 330–336.

Rodríguez-Castañeda AP, Sánchez-Rodríguez I, Shumilin E and Sapozhnikov D (2006) Element concentrations in some species of seaweeds from La Paz Bay and La Paz lagoon, south-western Baja California, Mexico. In Anderson R, Brodie J, Onsoy E and Critcheley AT (eds), *Eighteenth International Seaweed Symposium. Developments in Applied Phycology*, Vol. **1**. Dordrecht: Springer, pp. 173–182.

Rodríguez-Figueroa GM, Shumilin E and Sánchez-Rodríguez I (2009) Heavy metal pollution monitoring using the brown seaweed *Padina durvillaei* in the coastal zone of the Santa Rosalía mining region, Baja California Peninsula, Mexico. *Journal of Applied Phycology* **21**, 19–26.

Ryan S, McLoughlin P and O'Donovan O (2012) A comprehensive study of metal distribution in three main classes of seaweed. *Environmental Pollution* **167**, 171–177.

Sáez CA, Lobos MG, Macaya EC, Oliva D, Quiroz W and Brown MT (2012) Variation in patterns of metal accumulation in thallus parts of *Lessonia trabeculata* (Laminariales; Phaeophyceae): implications for biomonitoring. *PLoS ONE* **7**, 1–10.

Sánchez-Rodríguez I, Huerta-Díaz MA, Shoumilin E, Holguín-Quiñones O and Zertuche-González JA (2001) Elemental concentrations in different species of seaweeds from Loreto Bay, Baja California Sur, Mexico: implications for the geochemical control of metals in algal tissue. *Environmental Pollution* **114**, 145–160.

Sarada B, Prasad MK, Kumar KK and Murthy CVR (2014) Cadmium removal by macro algae *Caulerpa fastigiata*: characterization, kinetic, isotherm and thermodynamic studies. *Journal of Environmental Chemical and Engineering* **2**, 1533–1542.

Say PJ, Burrows IG and Whitton BA (1990) Enteromorpha as a monitor of heavy metals in estuaries. In McLusky DS, de Jonge VN and Pomfret J (eds), *North Sea – Estuaries Interactions. Developments in Hydrobiology*, Vol. **55**. Dordrecht: Springer, pp. 119–126.

Seeliger U and Edwards P (1977) Correlation coefficients and concentration factors of copper and lead in seawater and benthic algae. *Marine Pollution Bulletin* **8**, 16–19.

Servicio Geológico Mexicano (2008) Panorama minero del Estado de Baja California Sur. México: Secretaria de Economía, Servicio Geológico Mexicano, Coordinación General de Minería and Secretaría de Gobernación.

Serviere-Zaragoza E, Lluch-Cota SE, Mazariegos-Villarreal A, Balart EF, Valencia-Valdez H and Méndez-Rodríguez LC (2021) Cadmium, lead, copper, zinc, and iron concentration patterns in three marine fish species from two different mining sites inside the Gulf of California, Mexico. *International Journal of Environmental Research and Public Health* **18**, 844.

Shumilin E, Kalmykov S, Sapozhnikov D, Nava-Sánchez E, Gorsline D, Godinez-Orta L and Rodríguez-Castañeda A (2000) Major and trace element accumulation in coastal sediments along southeastern Baja California studied by instrumental neutron activation analysis and 210 Pb age-dating. *Journal of Radioanalytical and Nuclear Chemistry* **246**, 533–541.

Smith RD, Cameron KL, McDowell FW, Niemeyer S and Sampson DE (1996) Generation of voluminous silicic magmas and formation of mid-Cenozoic crust beneath north-central Mexico: evidence from ignimbrites, associated lavas, deep crustal granulites, and mantle pyroxenites. *Contributions to Mineralogy and Petrology* **123**, 375–389.

Soto-Jiménez MF, Hibdon SA, Rankin CW, Aggarawl J, Ruiz-Fernandez AC, Páez-Osuna F and Flegal AR (2006) Chronicling a century of lead pollution in Mexico: stable lead isotopic composition analyses of dated sediment cores. *Environmental Science and Technology* **40**, 764–770.

StatSoft (2007) *STATISTICA (Data Analysis Software System), Version 8.0*. Tulsa, OK: StatSoft, Inc.

Stengel DB, Macken A, Morrison L and Morley N (2004) Zinc concentrations in marine macroalgae and a lichen from western Ireland in relation to phylogenetic grouping, habitat and morphology. *Marine Pollution Bulletin* **48**, 902–909.

Storelli MM, Storelli A and Marcotrigiano GO (2001) Heavy metals in the aquatic environment of the Southern Adriatic Sea, Italy: macroalgae, sediments and benthic species. *Environment International* **26**, 505–509.

Strezov A and Nonova T (2003) Monitoring of Fe, Mn, Cu, Pb and Cd levels in two brown macroalgae from the Bulgarian Black Sea coast. *International Journal of Environmental Analytical Chemistry* **83**, 1045–1054.

Turner A, Pedroso SS and Brown MT (2008) Influence of salinity and humic substances on the uptake of trace metals by the marine macroalga, *Ulva lactuca*: experimental observations and modelling using WHAM. *Marine Chemistry* **110**, 176–184.

Vargas-González HH, Arreola-Lizárraga JA, García-Hernández J, Mendoza-Salgado RA, Zenteno-Savín T and Méndez-Rodríguez LC (2017) Calidad de sedimentos asociada a actividades antrópicas en lagunas costeras semiáridas subtropicales de la costa central este del Golfo de California. *Revista Internacional Contaminación Ambiental* **33**, 7–22.

Vasconcelos MTS and Leal MFC (2001) Seasonal variability in the kinetics of Cu, Pb, Cd and Hg accumulation by macroalgae. *Marine Chemistry* **74**, 65–85.

Vizzini S, Costa V, Tramati C, Gianguzza P and Mazzola P (2013) Trophic transfer of trace elements in an isotopically constructed food chain from a semi-enclosed marine coastal area (Stagnone di Marsala, Sicily, Mediterranean). *Archives of Environmental Contamination and Toxicology* **65**, 42–653.

Volterra L and Conti ME (2000) Algae as biomarkers, bioaccumulators and toxin producers. *International Journal of Environment and Pollution* **13**, 92–125.

Wedepohl KH (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta* **59**, 1217–1232.

Zar JH (2010) *Biostatistical Analysis*. Englewood Cliffs, NJ: Prentice-Hall.