

# Essential (Cu, Zn) And Nonessential Metals (Pb, Cd) In Muscle of Leopard Groupers (*Mycteroperca Rosacea*) From A Mining Port In The Gulf of California, Mexico: Human Health Risk Assessment

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## Research Article

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# Abstract

The concentrations of essential (Cu, Zn) and toxic (Cd, Pb) elements were quantified in the muscle of leopard groupers, *Mycteroperca rosacea*, in a mining district in the Gulf of California. Metal concentrations were analyzed by size, sex, maturity, season, year, and a risk factor for human consumption. Results indicated elevated levels of essential elements (Cu:  $11 \pm 34.3$   $\mu\text{g/g}$ , Zn:  $377 \pm 1390$   $\mu\text{g/g}$ ), up to 10 times higher than concentrations of toxic elements (Cd:  $0.06 \pm 0.1$   $\mu\text{g/g}$ , Pb:  $0.98 \pm 1.5$   $\mu\text{g/g}$ ). Cadmium was within permissible limit stated by Mexican norm (0.5  $\mu\text{g/g}$ ), but lead bordering its limit (1.0  $\mu\text{g/g}$ ). Heavy metal concentrations were comparable between males and females. Metal variations were not significantly correlated to the sex, maturity, season, or year ( $p > 0.05$ ). The evaluation of benefits (Daily Mineral Intake) and risks (Target Hazard Quotients) to health indicated that these fish did not represent adverse effects to the consumer, within worldwide limits, but the nutritional benefits are high.

## Introduction

The presence of heavy metals in marine ecosystems is one of the main contamination issues that leads to serious ecological and economic consequences (Ali and Khan 2019). Heavy metals are derived mainly from anthropogenic activities, such as dumping of residual waters and mining waste (Huerta-Díaz et al. 2014) which can contain persistent elements such as mercury (Hg), lead (Pb), and cadmium (Cd) with non-known biological function but considered potentially toxic elements, at even low concentrations (Ali and Khan 2019). Anthropogenic inputs related to mining waste can also contain copper (Cu) and zinc (Zn), essential micronutrients for numerous physiological functions (Xu et al. 2017; Rehman et al. 2019). However, if permissible limits are surpassed, these essential elements could also be harmful to human health. It is therefore recommended the nutritional and toxicological analysis of organisms in the human diets to assess the potential to benefit or health risk that represent for the population, mainly for children, pregnant women, and lactating mothers.

Marine species fish are an important component in human diets worldwide, because they contain essential amino acids, fatty acids (especially omega-3 and omega-6), protein, vitamins, and minerals (Pal et al. 2018). Thus, recommendations for the human diet include increasing the consumption of fish, due to fish fillets to 2 to 4 times per week can reduce the risk of cardiovascular diseases, diabetes, and obesity (FAO 2017). By 2016, the global *per capita* consumption of white fish (low in fat, rich in proteins and minerals) accounts 20.5 kg. White fish include fish species that represent approximately 90% of catches worldwide, such as tunas, snappers, and groupers (FAO 2017).

Many species of groupers are important commercial fish, and some of them are now used in other economic activities (e.g., aquaculture, sport fishing). In Mexico, the leopard grouper *Mycteroperca rosacea* (Streets 1877) is one of the most important species caught in the Gulf of California (Thomson et al. 2000). The annual production averaged 6,360 tons/year in 2014 and 2015, being the fourth species, in

terms of catch volume, after sardines, shrimp, and sharks (CONAPESCA 2014). Its meat is categorized as high-quality, reaching high prices in local (\$7–10 USD per kilo) and national markets.

Ecologically, leopard groupers are among the main predators in coastal environments (Craig and Hastings 2007). They occupy a high trophic level (~ 4.5) (Froese and Pauly 2021) with slow growth (from 15 to 21 years) (Díaz-Urbe et al. 2001), which makes them susceptible to accumulate high concentrations of heavy metals in tissues and organs. Overall, higher levels of heavy metals are usually associated with carnivorous and long-lived fish species (Evers et al. 2009). Despite its restricted distribution, high economic value, and scarce information on its biology, *M. rosacea* is no longer cataloged as “Vulnerable” by the International Union for the Conservation of Nature (IUCN) but currently cataloged as “Least concern” (Erisman and Craig 2018). Although non-changes in the leopard grouper populations have been reported over the past 30 years, enforcement in their population monitoring is required due to intense fishing pressure (Erisman and Craig 2018).

Fishing pressure on the leopard grouper occurs along the Gulf of California coastlines, however, their meat is local and nationally consumed. The objective of the present study was to evaluate the metal variability in function of fish biology (size, sex and maturity) and collection time (season and year). A second objective was to assess the potential human health benefit or risks related to concentrations of Cu, Pb, Cd, and Zn in the muscle tissue of the leopard grouper *M. rosacea*.

## Materials And Methods

### Study area and sample collection

Specimens of *Mycteroperca rosacea* were obtained in the port of Santa Rosalía (27° 20.353 'N; 112° 15.797' W), Baja California Sur, in the Gulf of California, Mexico (Fig. 1). Since 1885, this port has been extracting copper through the French mining company “Compagnie du Boleo, S.A.”. Currently, the company operates under the name “Minera y Metalúrgica del Boleo S.A. de C.V.” (Huerta-Díaz et al. 2014). About three million tons of accumulated slag are accumulated in the mine site, but unquantified amounts are already deposited on the adjacent marine environment (Shumilin et al. 2013; Huerta-Díaz et al. 2014). In addition to the mining industry, Santa Rosalía is height port for fishing and tourism vessels, and cargo and passenger ferries, and numerous small boats (Huerta-Díaz et al. 2014). The marine environment is, therefore, potentially polluted for heavy metals and marine organisms that inhabit the area, including the leopard grouper, being impacted.

Organisms were captured monthly (March 2014 to May 2015) by spearfishing while free diving, trying to obtain a good representation of different sizes. Specimens were stored on ice until processing at the Fish Ecology Laboratory at CICIMAR-IPN, where the total length (TL, cm) and weight (g) were recorded; sex was identified by direct observation of the gonads and later corroborated with histological analyses (Nikolsky 1963; Pérez-Olivas et al. 2018). Four maturity stages were considered according to Pérez-Olivas et al. (2018).

A total of 345 *M. rosacea* individuals was caught, with sizes ranging from 21 to 74 cm total length; 93 specimens were male and 185 were female. A total of 15 bisexual immature organisms, as well as, 52 individuals for which sex could not be histologically identified. These specimens were excluded in the comparative analyses by sex and maturity stages. According to fish size, the specimens were binned in small (n = 161, 47%), medium (n = 148, 43%), and large (n = 36, 10%). Besides, the specimens were categorized by caught season, in cold (n = 244, 71%) and warm season (n = 101, 21%), by year: 2014 (n = 180, 72%) and 2015 (n = 68, 27%).

Fish were dissected and the skin was removed to extract 5.0 g of muscle tissue from the anterior dorsal part of each individual. Each sample was tagged, stored in plastic bags, and frozen at -20°C.

### **Heavy metal analysis**

Muscle tissues samples were lyophilized at a 0.120 mBar pressure and -40°C for 72 h (Labconco, FreeZone 2.5). The water content (%) was calculated by weigh differences between fresh frozen and dried sample. The dried samples were ground using an agate mortar, homogenized, and packed into trace metal cleaned plastic vials.

Then, a lot of 248 composite muscle samples were sent to the Stable Isotope Laboratory at the ICMYL-UNAM at Mazatlán for the elemental analysis. Samples were processed and analyzed in HEPA filtered air (Class 1000), trace metal clean laboratory using high-purity reagents (trace metal grade) and water (18 MW cm<sup>-1</sup>; Milli-Q academic). Aliquots of fish muscle samples, blanks and certified reference material were digested in Teflon vials (Savillex) with 10 mL concentrated nitric acid (HNO<sub>3</sub>). Containers were then placed on mod-block unit (120°C) for 4 h. After digestion, samples were transferred to polyethylene vials and diluted with Milli-Q water to known volume (about 25 mL).

Elements were analyzed in a Thermo Scientific Element XR magnetic sector high-resolution inductively coupled plasma source mass spectrometry (HR-ICP-MS) (Soto-Jiménez et al. 2008). Accuracy of the analyses was determined with concurrent processing and analysis of certified reference material (CRM) Dog-Fish muscle (DORM-3) of Institute for National Measurement Standards of the National Research Council Canada. Recovery values of CRM for Cd was 92%, Cu 94%, Pb 88%, and Zn 92%. The detection limits were <6 ng g<sup>-1</sup> dry weight for Cd, <10 ng g<sup>-1</sup> for Pb, and <20 ng g<sup>-1</sup> for Cu and Zn. Concentrations of metals in fish were calculated in µg/g dry weight but reported as averages ± standard deviations in µg/g wet weight.

### **Toxicological evaluation**

The provisional tolerable weekly intake (PTWI) of Cu, Cd, Pb, and Zn (PTWI, in µg week<sup>-1</sup> kg<sup>-1</sup> of body weight) to establish the amount of leopard grouper fillet that the human population could consume without a health risk, was calculated by PTWI = [FAW] [MT] [PAW].

Where FAW is the average weight of fish fillet consumed by an adult (12 kg per person per year; De la O-Burrola et al. 2015), MT is the metal concentration ( $\mu\text{g} / \text{g}$ , w.w.) in muscle tissue of leopard grouper, and PAW is the average weight of the general population, considering women (pregnant and lactating) and children (4 to 6 years old).

Average worldwide weights established by the World Health Organization (e.g., 70 kg for men, 60 kg for women, and 16 kg for 4-6 year old children) and the average weights for the Santa Rosalía population (75 kg for men, 69 kg for women, and 18 kg for 4-6 year old children) (INEGI 2015) were taken into account. These average weights were also used for further evaluations.

The daily mineral intake of essential elements (Cu, Zn) was also calculated based on the consumption recommended by the Institute of Medicine of the National Academies of the United States ([www.iom.edu](http://www.iom.edu)), using the following equation:  $\text{DMI} = C * 100 / \text{RDI}$

Where DMI = daily mineral intake of essential elements, C = Cu or Zn concentration in 100 g of fresh fish weight, RDI = recommended daily intake, estimated as safe and adequate for each group in the population. CuRDI: men, women, and children = 900  $\mu\text{g} / \text{day}$ , pregnant and lactating women = 1000  $\mu\text{g} / \text{day}$ ; ZnRDI: men, women, pregnant, and lactating women = 40  $\mu\text{g} / \text{day}$ , children = 34  $\mu\text{g} / \text{day}$ . These values were estimated for a healthy population.

Additionally, the potential health risk due to harmful effects from long-term leopard grouper consumption (e.g., months or years) was calculated as the target hazard quotient, where high THQ values (>1) would represent a health risk. The THQ was calculated as follows:

$$\text{THQ} = \frac{\text{EF} * \text{ED} * \text{FIR} * \text{C}}{\text{RfD} * \text{BW} * \text{AT}}$$

Where C is the concentration of Cu, Pb, Cd, or Zn ( $\mu\text{g} / \text{g}$ ); EF is the exposure frequency (days/year); ED is the exposure duration (years/time); FIR is the fish intake rate (g/day); RfD is the daily fish intake rate (g/day); BW is the average body weight of the human population (kg); and AT is the average exposure time (days). All parameters except C, FIR, and BW were obtained from real data for the Santa Rosalía, BCS, Mexico population. The remaining data used in the formula were obtained from the FAO (2017), US EPA (2015), and Yi et al. (2011) and are shown in Table 1.

**Table 1** Parameters and values used for the THQ formula for each heavy metal

Factor	Definition	Unit	Value	Reference
EF	Exposure frequency	Days/year	365	Yi <i>et al.</i> (2011)
ED	Duration	Years	78	Yi <i>et al.</i> (2011)
FIR	Fish intake rate	g/day	32.8	
RfD	Reference dose	µg/kg/day	1.0E <sup>-01</sup> (Cd), 2.0E <sup>+01</sup> (Pb), 4.0E <sup>+01</sup> (Cu), 3.0E <sup>+02</sup> (Zn)	US EPA (2015)
BW	Average weight	Kg	70 ± 75	WHO; INEGI (2015)
AT	Average exposure time	Days	365*78 = 28.470	Yi <i>et al.</i> (2011)

Because heavy metal (Cu, Pb, Cd, and Zn) interactions can cause multiple effects (Gu *et al.*, 2017), we considered the added effect of these elements in the THQ as was proposed by Chien *et al.* (2002) and Gu *et al.* (2017), as shown in the following equation:

$$\text{Total THQ (TTHQ)} = \sum \text{THQ}_{\text{Cu,Pb,Cd,Zn}}$$

## Data analysis

Data were grouped by sex (males and females), maturity stages (stage 1, stage 2, stage 3 and stage 4) and size (small: <36 cm, medium: >36 cm and ≤51cm, large: >51 cm). Seasonality was defined according to temperature records for the study period obtained from MODIS-AQUA satellite images with 1.1 km resolution. Anomalies were recorded based on the annual average of 23°C (Moreno-Sánchez *et al.* 2019). Months with positive anomalies were assigned to the warm season and negative anomalies were assigned to the cold season. Simple linear regression (LR) analysis was carried to assess the association between the concentration of each heavy metal and the size of leopard groupers. Data base was split into categories (sex, maturity stages and season) and a LR of the heavy metal concentration as a function of size was fitted for each heavy metal and each category. With this analysis, the hypothesis that the b coefficient of the LR model was zero (e.g. no association between heavy metal concentration and size) was tested. All analyses were performed using packages found in R (R Core Team 2017).

## Results

### Heavy metal concentrations in muscle tissue

A summary of the heavy metal concentrations in muscle of leopard grouper *M. rosacea* caught in Santa Rosalía (average ± SD, maximum, and minimum), and the analysis comparative for sex, maturity stages, total length, and season is provided in Table 2. In agreement to the sex groups, males (Cu: 13.64 ± 33.64

$\mu\text{g/g}$ ; Zn:  $409.68 \pm 1348.08 \mu\text{g/g}$ ; Cd:  $0.08 \pm 0.20 \mu\text{g/g}$ ; Pb:  $0.84 \pm 1.0 \mu\text{g/g}$ ), females (Cu:  $12.77 \pm 39.93 \mu\text{g/g}$ ; Zn:  $417.40 \pm 1628.53 \mu\text{g/g}$ ; Cd:  $0.05 \pm 0.12 \mu\text{g/g}$ ; Pb:  $1.06 \pm 1.7 \mu\text{g/g}$ ) and hermaphrodites (Cu:  $7.74 \pm 7.75 \mu\text{g/g}$ ; Zn:  $164.75 \pm 219.94 \mu\text{g/g}$ ; Cd:  $0.07 \pm 0.10 \mu\text{g/g}$ ; Pb:  $0.79 \pm 1.3 \mu\text{g/g}$ ) showed comparable ranges for all metals. Because the comparable values and the high intravariability among sex groups, non-significant differences were observed.

Table 2

Heavy metal concentrations (mean  $\pm$  SD;  $\mu\text{g/g}$  wet weight) in *Mycteroperca rosacea* muscle in a mining port in the Gulf of California, Mexico

Category	<i>n</i>	Cu	Zn	Cd	Pb
Overall	248	11.6 $\pm$ 34.3 (0.01–361) <sup>c</sup>	377.3 $\pm$ 1389.9 (0.02–13165) <sup>c</sup>	0.06 $\pm$ 0.13 (0.001–1.13)	0.98 $\pm$ 1.56 (0.03–9.8) <sup>b</sup>
Sex					
Females	132	12.7 $\pm$ 39.9 (0.01–361) <sup>c</sup>	433.8 $\pm$ 1628.5 (0.02–13165) <sup>c</sup>	0.05 $\pm$ 0.12 (0.001–0.69)	1.06 $\pm$ 1.71 (0.03–8.9) <sup>a,b</sup>
Males	70	13.6 $\pm$ 33.6 (0.1–226) <sup>c</sup>	448.8 $\pm$ 1348 (0.01–9442) <sup>c</sup>	0.08 $\pm$ 0.2 (0.01–1.1)	0.84 $\pm$ 1.0 (0.02–9.8) <sup>b</sup>
Hermaphrodites	15	7.7 $\pm$ 7.7 (0.02–20) <sup>c</sup>	164.7 $\pm$ 219.9 (0.1–807) <sup>c</sup>	0.07 $\pm$ 0.1 (0.001–0.3)	0.79 $\pm$ 1.3 (0.02–5.3) <sup>b</sup>
Size					
Small	129	12 $\pm$ 34 (0.2–361) <sup>c</sup>	385 $\pm$ 1644 (0.1–13165) <sup>c</sup>	0.06 $\pm$ 0.1 (0.01–1.1)	0.98 $\pm$ 1.6 (0.1–9.8) <sup>b</sup>
Medium	99	11 $\pm$ 32 (0.01–361) <sup>c</sup>	328 $\pm$ 1269 (0.02–13165) <sup>c</sup>	0.06 $\pm$ 0.1 (0.01–0.7)	1.0 $\pm$ 1.5 (0.02–9.8) <sup>a,b</sup>
Large	20	7 $\pm$ 32 (0.2–90) <sup>c</sup>	246 $\pm$ 1330 (0.8–6901) <sup>c</sup>	0.03 $\pm$ 0.07 (0.01–0.1)	0.86 $\pm$ 1.4 (0.05–2.7) <sup>b</sup>
Maturity stage					
Maturity stage 1	141	18.1 $\pm$ 58.4 (0.3–283) <sup>c</sup>	588 $\pm$ 2394 (2.3–12006) <sup>c</sup>	0.1 $\pm$ 0.2 (0.01–0.8) <sup>a,b</sup>	1.5 $\pm$ 2.4 (0.07–15.4) <sup>a,b</sup>
Maturity stage 2	47	16.8 $\pm$ 55.6 (0.3–123) <sup>c</sup>	517.9 $\pm$ 2256 (6.0–5767) <sup>c</sup>	0.1 $\pm$ 0.2 (0.01–1.3) <sup>a,b</sup>	1.5 $\pm$ 2.4 (0.06–11.0) <sup>a,b</sup>
Maturity stage 3	76	13.8 $\pm$ 56.7 (0.3–664) <sup>c</sup>	430.2 $\pm$ 2323 (3.7–24197) <sup>c</sup>	0.1 $\pm$ 0.2 (0.01–0.9) <sup>a,b</sup>	1.4 $\pm$ 2.3 (0.06–6.5) <sup>a,b</sup>

<sup>a</sup>Values above recommended limits set by the official Mexican norm NOM-242-SSA1-2009 (Cd 0.5 and Pb 1.0  $\mu\text{g/g}$  w.w.); <sup>b</sup>US-EPA, FDA criterion, surpassing established limits of 0.5 for Cd and 0.5 for Pb; <sup>c</sup>United Kingdom norm (UK-EEA food standards) of Zn 50 and Cu 5  $\mu\text{g/g}$  w.w.

Category	<i>n</i>	Cu	Zn	Cd	Pb
Maturity stage 4	8	14.1 ± 58.1 (0.6–132) <sup>c</sup>	447.3 ± 2362 (12.2–2231) <sup>c</sup>	0.1 ± 0.2 (0.02–0.1) <sup>a,b</sup>	1.6 ± 2.5 (0.05–1.7) <sup>a,b</sup>
Season					
Warm season	80	2.0 ± 3.0 (0.2–23)	50 ± 66 (0.8–411) <sup>c</sup>	0.01 ± 0.03 (0.02–0.11)	1.0 ± 2.0 (0.05–9.8) <sup>a,b</sup>
Cold season	168	16 ± 35 (0.1–361) <sup>c</sup>	539 ± 1412 (0.1–13165) <sup>c</sup>	0.11 ± 0.15 (0.01–1.1) <sup>a,b</sup>	1.0 ± 1.6 (0.02–8.9) <sup>a,b</sup>
Year					
2014	180	8.8 ± 31.5 (0.17–361) <sup>c</sup>	251 ± 1239 (0.1–13165) <sup>c</sup>	0.08 ± 0.2 (0.02–1.1)	0.97 ± 1.6 (0.03–9.9) <sup>b</sup>
2015	68	26 ± 38.4 (0.2–205) <sup>c</sup>	867 ± 1499.7 (5.1–8702) <sup>c</sup>	0.2 ± 0.3 (0.1–1.1) <sup>b</sup>	1.5 ± 1.9 (0.1–1.9) <sup>a,b</sup>
<sup>a</sup> Values above recommended limits set by the official Mexican norm NOM-242-SSA1-2009 (Cd 0.5 and Pb 1.0 µg/g w.w.); <sup>b</sup> US-EPA, FDA criterion, surpassing established limits of 0.5 for Cd and 0.5 for Pb; <sup>c</sup> United Kingdom norm (UK-EEA food standards) of Zn 50 and Cu 5 µg/g w.w.					

Heavy metal concentrations in maturity stages were, stage 1 (Cu: 18.1 ± 58.4 µg/g; Zn: 588 ± 2394 µg/g; Cd: 0.1 ± 0.2 µg/g; Pb: 1.5 ± 2.4 µg/g), stage 2 (Cu: 16.8 ± 55.6 µg/g; Zn: 517.9 ± 2256 µg/g; Cd: 0.1 ± 0.2 µg/g; Pb: 1.5 ± 2.4 µg/g), stage 3 (Cu: 13.8 ± 56.7 µg/g; Zn: 439.2 ± 2323 µg/g; Cd: 0.1 ± 0.2 µg/g; Pb: 1.4 ± 2.3 µg/g) and stage 4 (Cu: 14.1 ± 58.1 µg/g; Zn: 447.3 ± 2362 µg/g; Cd: 0.1 ± 0.2 µg/g; Pb: 1.6 ± 2.5 µg/g). There were non-significant differences in maturity stages between metals levels.

Regarding size, the metal levels were orders as follow, small fish (Cu: 12 ± 34 µg/g; Zn: 385 ± 1644 µg/g; Cd: 0.06 ± 0.1 µg/g; Pb: 0.98 ± 1.6 µg/g), then medium-sized fish (Cu: 11 ± 32 µg/g; Zn: 328 ± 1269 µg/g; Cd: 0.06 ± 0.1 µg/g; Pb: 1.0 ± 1.5 µg/g) and large specimens presented lower concentrations (Cu: 7.0 ± 32 µg/g; Zn: 246 ± 1330 µg/g; Cd: 0.03 ± 0.07 µg/g; Pb: 0.86 ± 1.4 µg/g). Non-significant differences were observed among size groups.

An analysis comparative related to the collection time, showed that the heavy metal concentrations in organisms collected in 2015 (Cu: 26 ± 38.4 µg/g; Zn: 867 ± 1499 µg/g; Cd: 0.2 ± 0.3; Pb: 1.5 ± 1.9 µg/g) were significantly higher ( $p < 0.05$ ) than 2014 specimens (Cu: 8.8 ± 31.5 µg/g; Zn: 251 ± 1239 µg/g; Cd: 0.08 ± 0.2 µg/g; Pb: 0.97 ± 1.6 µg/g). Besides, significant differences ( $p < 0.05$ ) were observed for Cu, Zn and Cd between warm (Cu: 2.0 ± 3.0 µg/g; Zn: 50 ± 66 µg/g; Cd: 0.01 ± 0.03 µg/g) and cold season (Cu: 16 ± 35 µg/g; Zn: 539 ± 1412 µg/g; Cd: 0.11 ± 0.15 µg/g), but not for lead (warm: 1.0 ± 2.0 µg/g; cold: 1.0 ± 1.6 µg/g).

Results of the fitted simple linear regression (LR) suggested that the association between heavy metal concentration in muscle and size of leopard groupers is weak (low  $R^2$  values) and non significant ( $p(b = 0) > 0.05$  in all cases) (Table 3).

Table 3

Coefficient values of the linear regression of variations by sex, maturity stages and season in the muscle of leopard grouper *Mycteroperca rosacea* in Santa Rosalía, BCS, Mexico

Variables	Linear regression coefficients					
	<i>n</i>	R <sup>2</sup>	<i>b</i>	<i>a</i>	p( <i>a</i> = 0)	p( <i>b</i> = 0)
Cu						
F	132	0.004	0.3	2047030	1	0.46
M	69	0.01	0.4	-2975734	0.87	0.36
Maturity stage 1	141	0.01	0.5	-1018392	0.97	0.45
Maturity stage 2	47	0.02	-0.48	26628406	0.02	0.14
Maturity stage 3	76	0.01	0.6	-11830348	0.74	0.43
Maturity stage 4	8	0.14	2688	-76258327	0.48	0.40
Cold	148	0.01	0.5	-2897376	0.85	0.19
Warm	47	0.05	-0.1	6542092	0.01	0.12
Pb						
F	132	0.0005	-0.005	13403743	0.07	0.79
M	69	0.04	0.02	-0.1501317	0.75	0.07
Maturity stage 1	141	0.007	-0.02	19128.434	0.03	0.39
Maturity stage 2	47	0.105	0.07	-18344799	0.24	0.06
Maturity stage 3	76	0.04	0.02	-0.1766029	0.77	0.13
Maturity stage 4	8	0.11	0.03	-0.7844367	0.62	0.45
Cold	148	0.0004	-0.003	11716741	0.03	0.80
Warm	47	0.01	0.02	-0.1538668	0.90	0.42
Cd						
F	132	0.02	-0.002	0.138755835	0.002	0.06
M	69	0.005	0.001	0.010781516	0.92	0.54
Maturity stage 1	141	0.03	-0.002	0.158315518	0.002	0.05
Maturity stage 2	47	0.001	0.001	0.088152186	0.74	0.83
Maturity stage 3	76	0.003	0.0005	0.007955513	0.89	0.70
Maturity stage 4	8	0.14	0.002	-0.077131024	0.49	0.40

Variables	Linear regression coefficients					
	<i>n</i>	R <sup>2</sup>	<b>b</b>	<b>a</b>	p(a = 0)	p(b = 0)
Cold	148	0.001	-0.0006	0.100902619	0.10	0.69
Warm	47	0.02	-0.0005	0.044550624	0.02	0.27
Zn						
F	132	0.01	252802895	-48738201	0.43	0.13
M	69	0.009	151811566	-15627183	0.83	0.42
Maturity stage 1	141	0.008	-127235772	74047734	0.12	0.35
Maturity stage 2	47	0.005	87707420	9110244	0.91	0.67
Maturity stage 3	76	0.01	302079514	-62109127	0.65	0.37
Maturity stage 4	8	0.13	453892443	-129630397	0.48	0.41
Cold	148	0.02	297236154	-53587711	0.38	0.07
Warm	47	0.02	0.69	1298858	0.62	0.31

A comparison of metal concentrations found in the grouper muscle samples, evidenced that the essential elements (Cu =  $11.61 \pm 34.36 \mu\text{g/g}$  and Zn =  $377.33 \pm 1389.98 \mu\text{g/g}$ ) showed global values that exceeded the norms set by the United Kingdom (UK-EEA food standards Cu:  $5.0 \mu\text{g/g}$ ; Zn:  $50 \mu\text{g/g}$ ), whereas Cd, a non-essential element (Cd =  $0.06 \pm 0.13 \mu\text{g/g}$  vs Cd =  $0.05 \mu\text{g/g}$ ) were within ranges established by NOM-242 (Table 2). In the case of Pb, the global average is bordering the limit established by NOM-242. Even, a numerous number of samples ( $n = 114$ , 46%) are above the limit of  $1 \mu\text{g/g}$ .

### Ecotoxicological evaluation

According to the Calculations of the maximum weekly intake values (MWIV) for Cd values, we suggest that children under 6 years can consume fish fillets of up to approximately 533 g per week and that women and men can consume up to 2,000 g of leopard grouper. However, Pb values indicated that the frequency of leopard grouper consumption should decrease. The average values of the risk coefficient ( $\text{THQ}_{\text{Cu}}: 0.1 \pm 0.3$ ,  $\text{THQ}_{\text{Pb}}: 0 \pm 0.1$ ,  $\text{THQ}_{\text{Cd}}: 0.3 \pm 1.4$ ,  $\text{THQ}_{\text{Zn}}: 0.2 \pm 0.6$ ) showed there was no risk from leopard grouper ingestion; however, the maximum range of  $\text{THQ}_{\text{Cd}}$  values could surpass established limits ( $> 1$ ). In contrast, the suggested amounts of essential elements (Cu and Zn) were higher for the three human population groups (children, women, and men).

The benefits that consumption of this fish provide for vulnerable groups in the population (children, pregnant, and lactating women) indicated that each 100 g of leopard grouper filet represented over 1% of Cu and 100% of Zn. The percentages of Cu daily mineral intake oscillated between 1.2 and 1.3, while the percentages of Zn daily mineral intake ranged from 943 to 1,110.

## Discussion

The leopard grouper *Mycteroperca rosacea* is one of the main predatory species on rocky reefs (Thomson et al. 2000; Moreno-Sánchez et al. 2019). Due to its carnivorous habits and slow growth (Díaz-Uribe et al. 2001), it can be susceptible to accumulating high levels of heavy metals, as occurs with other species with these characteristics, such as *Scomberomorus sierra*, *Nematistius pectoralis*, *Caulolatilus princeps*, and *Lutjanus colorado* (Frías-Espericueta et al. 2010; Ruelas-Inzunza et al. 2010, 2014). However, Cd concentrations (0.06 µg/g) were below the limit set by the Mexican norm NOM-242, whereas Pb concentrations found in *M. rosacea* muscle tissue (0.98 µg/g) were on average close to the limit set by the Mexican norm (Pb: 1.0 µg/g; Cd: 0.5 µg/g). The average values of essential metals (Cu: 11.61 ± 34.36 µg/g; Zn: 377.33 ± 1389.98 µg/g) were well above the maximum criteria allowed by international regulations (UK-EEA food standards Cu: 5.0 µg/g; Zn: 50 µg/g).

Levels of Cd (0.2 µg/g) and Pb (2.5 µg/g) one to three times higher than those recorded here for *M. rosacea* have been recorded in other commercially important species in Sinaloa, Mexico (*S. sierra*, *C. princeps*, and *L. colorado*). Coastal ecosystems in Sinaloa has a significant anthropogenic influence, raw or partially process effluents of aquaculture, agriculture, food processing industry, urban wastewater and fisheries converge (Frías-Espericueta et al. 2010; Ruelas-Inzunza et al. 2014). Concentrations of Cu, Zn, Pb, and Cd above the limits established in the sediment quality criteria (Cu: 3,860, Zn: 2,600, Pb: 240, Cd: 240 mg/kg) have been reported in the Central Gulf of California (in Santa Rosalía). Cooper mining activities carried out in Santa Rosalía maritime port, since beginning 19th century to the present, are the most important source of heavy metals to the adjacent coastal region (Jonathan et al., 2016). Although isolated cases of inputs of several contaminants are fundamental in explaining the presence of heavy metals in organisms (Zhang et al. 2017; Ali and Khan 2019), the concentrations of Pb and Cd found in *M. rosacea* do not reflect those inputs. However, the concentrations of essential elements such as Cu (11.6 µg/g) reported for *M. rosacea* in the Gulf of California were five times higher than what was reported in Sinaloa for other fish such as *L. colorado* (Cu: 2.1 µg/g).

Organisms that feed mainly on invertebrates, present lower heavy metal levels than those who include a greater proportion of fish in their diet (Escobar-Sánchez et al. 2016; Murillo-Cisneros et al. 2018; Sujitha et al. 2019). *M. rosacea* is a predator that feeds mainly on the euphausiid *Nyctiphanes simplex*, which comprises 65% of the diet, in terms of relative importance (Moreno-Sánchez et al. 2019). Therefore, it should be expected that due to the type of feeding shown by *M. rosacea*, average heavy metal concentrations would be at the limit (Pb) and/or below the limit (Cd) set by NOM-242-SSA-2009.

Other variables such as size and sex could have an effect on the bioaccumulation of heavy metals (Xia et al., 2019). For example, some elements such as Hg and Cd have shown a positive relationship with fish size (Tremain and Adams 2012; Ruelas-Inzunza et al. 2014), where there were greater heavy metal concentrations at greater fish sizes. This was reported for other grouper species (*Epinephelus*, *Mycteroperca*, and *Cephalopholis*) (Tremain and Adams 2012). However, this correlation was not directly proportional with growth (in size, age, or weight) for other heavy metals such as Pb, Zn, and Cu (García-

Hernández et al. 2007; Rodrigues et al. 2018; Xia et al. 2019). In this study, there was no evident relationship between total length and the analyzed heavy metals. García-Hernández et al. (2007) showed that the lack of correlation between size and heavy metal concentrations (Hg, specifically) can be related to different fish species feeding on the same food components.

*Nyctiphanes simplex* is the main *M. rosacea* prey in Santa Rosalía, however, this grouper can vary the proportion of food items in its diet according to size (Moreno-Sánchez et al. 2019). For example, small-sized grouper (< 36 cm; *n*: 129) fed exclusively on euphausiids (*N. simplex*), whereas medium-sized fish (> 36 cm < 51 cm; *n*: 99) had a mixed diet (invertebrates and fish), and large organisms (> 51 cm; *n*: 20) consumed a greater proportion of fish (*S. sagax*, *Microlepidotus inornatus*, *Chromis atrilobata*) (Moreno-Sánchez et al. 2019). As mentioned previously, this would imply that large organisms would present greater heavy metal concentrations (Murillo-Cisneros et al. 2018). However, despite the fact that differences in the diet were reflected in the heavy metal concentrations by size (small, medium, and large), the greatest heavy metal concentrations were recorded in the small and medium-sized organisms (see Table 2) and not in the largest ones. Sujitha et al. (2019) reported that in different crustacean species (e.g., *Panulirus interruptus*, *Penaeus stylirostris*) high Zn (> 80 µg/g) and Cu (> 45 µg/g) levels occurred, which could explain the presence of greater quantities of those elements in smaller *M. rosacea*.

The occurrence of greater Cu and Zn concentrations in small-sized fish could be due to small individuals showing accelerated growth in their first years of life (1 to 3 years), as these elements are metabolically required to carry out necessary physiological processes. Moreover, the elimination rate of toxic metals is more efficient (Rajeshkumar and Li 2018). The size at first maturity of *M. rosacea* has been estimated at 40.7 cm total length (Pérez-Olivas et al. 2018), which coincides with essential element concentrations being greater in small and medium-sized fish. That is, it should be expected that groupers of this size should have higher heavy metal levels, because Cu and Zn are important micronutrients for gonad maturation and are necessary to carry out reproductive events successfully (Jeziarska et al. 2009). We suggest that the low Pb and Cd levels recorded could be due to more efficient elimination at those sizes (Yi and Zhang 2012), at least in *M. rosacea*.

The high levels of Pb and Cd by the all maturity stages denote increased metabolic activity and high lipid content of the gonads that stimulate rapid accumulation of lipophilic metallic species and are associated to the metallothionein synthesis in the liver (El-Greisy and El-Gamal 2015). The metallothionein proteins binds to metals such Cd forms a non-toxic complex that is retained in the tissue, resulting in bioaccumulation process. This induction showed that sexual maturity helps to understand the bioavailability of the metals and detoxification of both essential and nonessential metals (Hemmadi 2016).

Compared with what was reported for the El Niño event of 1997 and 1998, the El Niño phenomenon of 2015 was characterized as being the most intense event recorded, with temperatures over 0.76° higher than the previous record (Pérez-Olivas et al. 2018). Because of this, there was a difference of 2.2°C between 2014 and 2015. This difference was reflected in the metal concentrations, with greater

concentrations in 2015 (Cu: 26 µg/g, Zn: 867 µg/g, Cd: 0.2 µg/g, Pb: 1.5 µg/g) than in 2014 (Cu: 8.8 µg/g, Zn: 251 µg/g, Cd: 0.08 µg/g, Pb: 0.97 µg/g). These increases in heavy metal concentrations coincide with what was reported by Huerta-Díaz et al. (2014) for the same study area, regarding high heavy metal levels resulting from the mixing and removal of particulate materials in marine sediments, caused by natural phenomena such as hurricanes and storms.

In 2014, hurricane “Odile” impacted Baja California Sur (CONAGUA 2014) in the months categorized as the warm season, coinciding with enrichment in heavy metals during the previously mentioned phenomena. Therefore, the heavy metal enrichment observed in 2015 could be reflecting the impact of that hurricane, which entrained heavy metals through pluvial precipitation and temporary streams flowing into the port. Other activities carried out in Santa Rosalía are not dismissed, where a combination of environmental factors as well as port operations could increase heavy metal concentrations. This increase has also been reported in other heavy metal studies in Northwestern Mexico (Frías-Espericueta et al. 2010; Ruelas-Inzunza et al. 2010; 2014).

Heavy metals are a potential problem in areas close the coast and constitute a human health risk. However, there is currently a discrepancy between recommendations by public health sectors (FAO 2017) and studies that advise reducing the consumption of fish fillet; additionally, the fish consumption by the population is underestimated because the frequency of consumption of fish in coastal communities is often much greater than reported.

In the present study, a consumption of approximately 700 g does not represent a risk to health. However, the frequency of leopard grouper consumption by the population of Santa Rosalía was greater than what could be recommended here (CONAPESCA 2015). Essential elements such as Cu and Zn are required for the correct absorption of vitamins B<sub>6</sub>, B<sub>12</sub>, C, and A, among others, especially in vulnerable groups (children, pregnant women, and lactating women) who require special care to avoid problems of nutrition and embryonic development. According to daily mineral intake values, the *M. rosacea* fillet is highly recommended and beneficial to the population; nutritional values are high and meet levels indicated at worldwide levels (FAO 2017) and are even higher than what has been reported for other fish in Northwestern Mexico (Frías-Espericueta et al. 2010).

The risk factor (THQ) showed no adverse long-term effects, whereas Cd should be considered with caution due to the maximum values obtained. In the present study, we suggest continuous monitoring of Cd levels to evaluate more in depth the THQ and consider later years, because estimated values correspond to 2014 and 2015.

## Conclusion

This is the first study focusing on heavy metals in *Myteroperca rosacea*. Results on metal concentrations suggest that although the samples of leopard groupers (*M. rosacea*) come from an area next to mining district “El Boleo” in Santa Rosalía, Mexico, no essential metals (Cd and Pb) were below the limit set by

the EPA, FDA, and Mexican norm (NOM-242). Further monitoring is needed for Pb, due to its average was close to the limit set by the Mexican norm. The leopard grouper did not represent adverse effects to the consumer, in contrast, the nutritional benefits are high. Enrichment in heavy metals during warm season may be attributed to impact of natural phenomenon (hurricane) on the study area. *Mycteropeca rosacea* is still being fished and marketed, therefore it is important to know the ingestion rate of this species in Mexico to understand metal impacts on human populations.

## Declarations

### Ethics approval and consent to participate

Not applicable. This manuscript does not contain any studies with human participants or animals performed by any of the authors.

### Consent for publication

Not applicable

### Availability of data and materials

Not applicable

### Competing interest

The authors declare that they have no conflict of interest.

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### Autor contribution

Marina S. Irigoyen-Arredondo: Conceptualization, Data analysis, Writing- Original draft preparation. Xchel G. Moreno-Sánchez: Conceptualization, Visualization, Investigation. Ofelia Escobar-Sánchez: Funding acquisition, Project administration, Data curation, Writing- Reviewing and Editing. Martín F. Soto-Jiménez: Data curation, Writing- Reviewing and Editing. Emigdio Marín-Enríquez: Software. L. Andrés Abitia-Cárdenas: Conceptualization, Supervision, Investigation, Funding acquisition.

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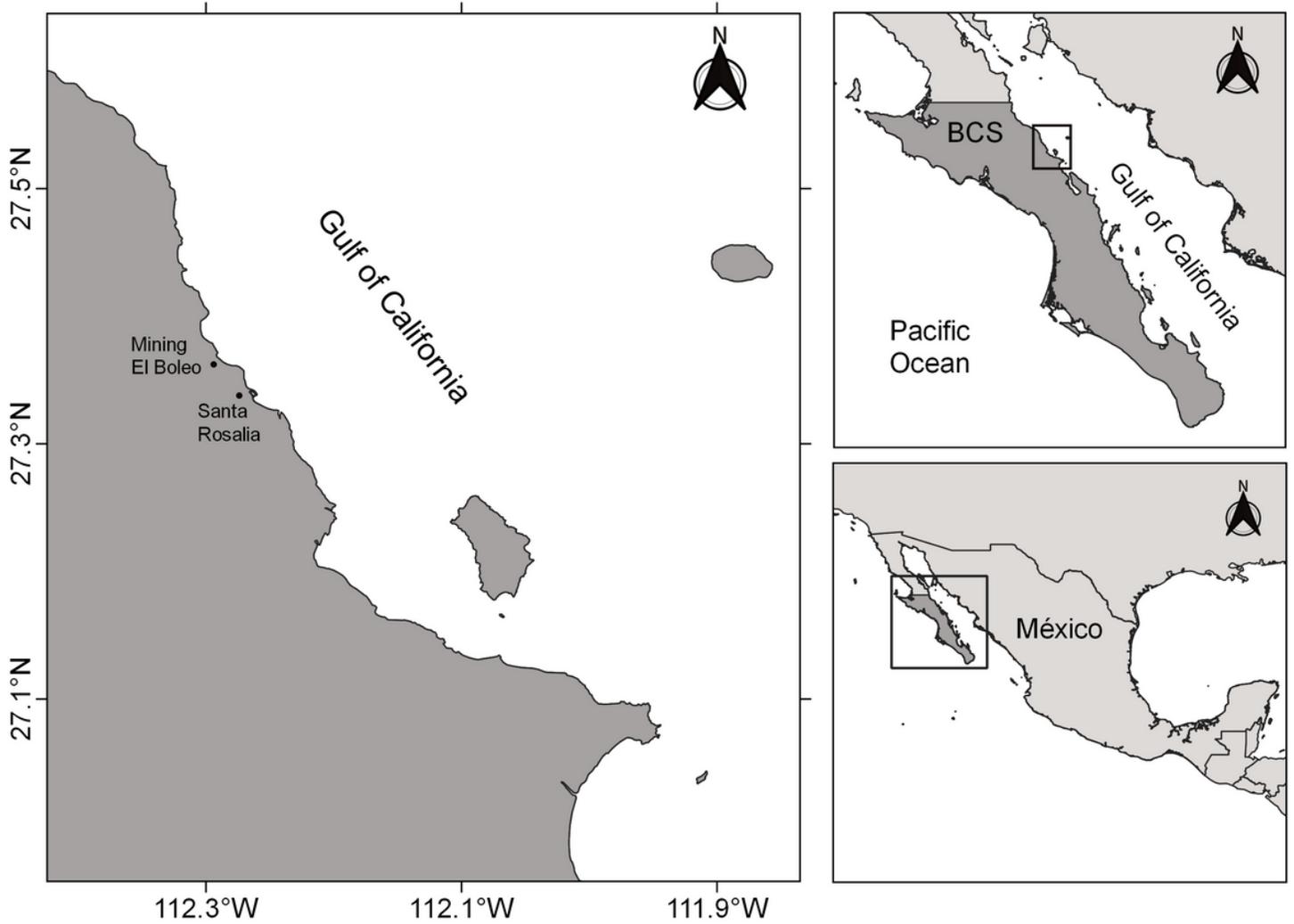
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## Figures



**Figure 1**

Geographic location of the port of Santa Rosalía, Baja California Sur, Mexico.

## Supplementary Files

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