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Bioaccumulation and biomagnification of potentially toxic elements in the octopus *Octopus hubbsorum* from the Gulf of California

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A B S T R A C T

The concentrations of 21 potentially toxic elements (PTEs) were determined in the tissues of *Octopus hubbsorum* from three locations along the Gulf of California coast: two near Santa Rosalia (SR), a site with historical metal contamination, and one in La Paz Bay, a reference site. Concentrations of Cd, Co, Cr, Mn, Ni, Pb, and Zn in octopus from the two SR sites were higher than those from the reference site, reflecting the higher sediment concentrations at the mining-impacted locations. The highest bioaccumulation and biomagnification of elements was found in digestive gland and branchial hearts, while the lowest was observed in the mantle, where the mean concentration of PTEs did not exceed international standards for human consumption of octopus. This study found elevated PTEs in octopus from sites with high metal contamination, and presents the first data on these elements in octopus from the Gulf of California.

1. Introduction

Octopus is a high-demand fishery for human consumption throughout the world (FAO, 2016). However, similar to other cephalopods, they have the ability to bioaccumulate high concentrations of potentially toxic elements (PTEs) in their tissues, posing a risk to their consumers (e.g. Napoleão et al., 2005; Rjeibi et al., 2014). For this reason, understanding PTEs in these organisms has become a topic of growing international interest (e.g. Raimundo et al., 2010a; Semedo et al., 2012; Grayson and Sekadende, 2014; Karim et al., 2016).

In marine ecosystems, octopuses play a key role in the transfer of contaminants through food webs (Bustamante et al., 1998a). They feed upon crustaceans and molluscs (FAO, 2016) that accumulate high concentrations of metals and other elements (Jakimska et al., 2011), and are known to accumulate potentially toxic elements (PTEs) such as Cd and As (Seixas et al., 2005a). Octopuses are also part of the diet of many predators including fishes, marine mammals and seabirds, so they act as vectors in the transfer of PTEs to higher trophic levels (Bustamante et al., 1998a, b).

The bioaccumulation of PTEs in octopus occurs differentially in the various organs and tissues, with the digestive gland and branchial hearts as the main storage and detoxification sites (Nessim and Riad, 2003; Raimundo and Vale, 2008; Raimundo et al., 2010a). Other tissues such as the mantle and arms - the only parts consumed by humans - generally have lower concentrations (e.g. Napoleão et al., 2005; Raimundo and Vale, 2008). However, there are reports that the mantle and arms of octopus exceed the maximum PTE content in international standards for human consumption, posing a risk for human health (Rossi et al., 1993; Grayson and Sekadende, 2014).

In Mexico, the octopus fishery on the Pacific coast is mainly based on the capture of a single species: *Octopus hubbsorum* (López-Uriarte et al., 2005). Within the Gulf of California, the most important location for this fishery is the Santa Rosalia mining port (López-Uriarte et al., 2005), a site known to have potentially toxic levels of metals in coastal marine sediments (Shumilin et al., 2013).

Despite their potential to affect human and ecosystem health, to date there are no studies evaluating PTE concentrations in octopus from Santa Rosalia, nor in any octopus species inhabiting coastal areas of the American continent. The objectives of this research were to determine: (1) the bioaccumulation of PTEs in four tissues of *Octopus hubbsorum*: mantle, branchial hearts, digestive gland, and gills; and (2) the biomagnification of these elements, if any, by analyzing one of its potential

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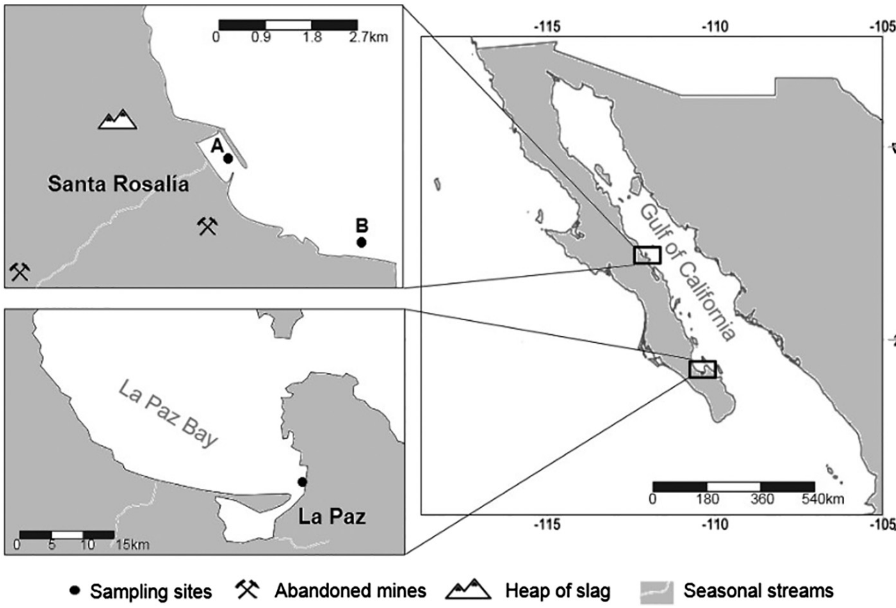

Fig. 1. Sampling sites of *Octopus hubbsorum* on the Gulf of California: two sites near Santa Rosalía (A and B) with historical metal contamination in marine sediments, and one in La Paz Bay, as a reference site.

prey, the clam *Megapitaria squalida*, collected from the Santa Rosalia mining port. Results from the mining-impacted sites were compared to the same species from La Paz Bay, BCS, Mexico, a reference site.

2. Materials and methods

2.1. Study area

Santa Rosalia is a fishing port located in the central part of the Gulf of California's western coast, Mexico (Fig. 1). The local climate is arid, with a mean temperature of 23.4 °C, and scarce rainfall, with annual mean precipitation of 117.2 mm (Volke-Sepúlveda et al., 2003). It is a location with a long history of mining activity related to copper extraction from “El Boleo” field (1885–1985), so that the local coastal sediments are highly polluted by metals, mainly Mn, Cu, Zn, Pb, Co, U and Cd (Shumilin et al., 2013). The concentrations of these elements are so high that they are potentially toxic for marine biota (Shumilin et al., 2013). Specifically, Cu concentrations exceeded the effect range medium (ERM) by up to 17-fold, which translates into a potential negative biological effect for 50% of marine organisms (Shumilin et al., 2011). The local mussels *Modiolus capax* (Gutiérrez-Galindo et al., 1999; Muñoz-Barbosa and Huerta-Díaz, 2013) and *Mytilus edulis* (Cadena-Cárdenas et al., 2009) have Cu concentrations up to 11 times higher than those from other areas of the Baja California peninsula; both bivalve species are part of the diet of *O. hubbsorum* (López-Uriarte et al., 2010).

2.2. Sampling

Cd, Co, Cu, Mn, Pb, and Zn levels in Santa Rosalia marine sediments show a marked decreasing gradient toward the port's most remote areas (Shumilin et al., 2011, 2013). Accordingly, sampling was conducted in two locations: at (A) the area closest to the port dock (Hot spot zone), where the highest sediment concentrations of these elements have been recorded, and at (B) an area located 2 km to the south, where lower sediment concentrations have been found (Fig. 1). In addition, reference samples were collected from El Caimancito, La Paz Bay. This site is 400 km south of Santa Rosalia and sediment metal concentrations here are related mainly to the regional geology and deemed typical of pristine environments with no anthropogenic impact; the effects of the closest mining area (the mining company Roca Fosfórica Mexicana “Rofomex”) are localized (Rodríguez-Castañeda et al., 2006) (Fig. 1).

Twenty three *O. hubbsorum* specimens were collected from the following locations: Santa Rosalia A (n = 8), Santa Rosalia B (n = 7) and La Paz Bay (n = 8). Specimens were caught by artisanal fishermen in October 2015 and June 2016. To avoid any potential bias from individuals of extreme size or weight, all octopuses were within a similar range of size and weight. Specimens were transported in sea water with ice to reduce their metabolic rate and minimize the mobilization of PTEs between organs and tissues (Martin and Flegal, 1975). Immediately after being killed, the sex, total weight (TW), total length (TL), and dorsal mantle length (DML) were determined. The mantle (mantle and arms are the main tissues consumed by humans but mantle is more frequently used in similar studies), digestive gland (main storage tissue), branchial hearts (main detoxification tissue) and gills (tissue with major interaction with water and exposed to the waterborne contamination) of each specimen was removed. Each tissue was carefully washed with deionized water, weighed (± 0.1 g), frozen (− 20 °C), freeze-dried (− 30 °C and 100 m Torr), powdered and homogenized in agate mortars for analysis. To minimize the risk of contamination, organisms and samples were handled only with acrylic and plastic materials previously washed with deionized water and Milli-Q(R) metal-free water with 5% nitric acid. Analyses were performed in the Canadian Rivers Institute at the University of New Brunswick, NB, Saint John, Canada.

2.3. Determination of potentially toxic elements

Using between 0.001 and 0.02 g (dry weight) of each sample, total Hg (THg) was determined by thermal decomposition, amalgamation and thermal absorption, with a Milestone DMA-80 direct mercury analyzer. Quality assurance was assessed every 10 samples using a blank (< 0.00250 mg kg^{-1} limit of detection), a duplicate (relative percent difference $<$ 20%), a mussel tissue certified reference material SRM 2976 and an internal reference material (recovery percentages between 80 and 120%). The limit of detection (LOD) was determined using 3 × the SD of the blanks run over the project plus the average of the blanks (see Table 1).

For the determination of Ag, Al, As, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn, approximately 0.5 g (dry weight) of each sample was digested with 10 mL of concentrated nitric acid (HNO_3) in a CEM MARS5 microwave digester for approximately 1 h. Then, each sample was diluted in 40 mL Milli-Q(R) metal-free water, and was analyzed by inductively coupled plasma optical emission