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Trace elements in marine organisms of Magdalena Bay, Pacific Coast of Mexico: Bioaccumulation in a pristine environment

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Abstract Trace element (Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd, As, Hg) concentrations were assessed in marine organisms ($n = 52$) sampled from the Magdalena Bay lagoon complex in Baja California Sur, Mexico, a pristine marine environment. The overall trend of metal concentrations (dry weight) in the organisms was found to be Fe > Zn > Cd > Cu > Mn > Pb > As > Hg > Ni > Cr > Co. Bivalve mollusks (53.83 mg kg^{-1}) contained twofold higher levels of metals than the finfishes (20.77 mg kg^{-1}). Calculated BioConcentration Factor (BCF) values showed that dissolved Mn is readily bioavailable to the organisms, whereas Biota Sediment Accumulation Factor (BSAF) indicated high values for Zn, Cu and Cd. Cd and As levels were observed to be increasing with the trophic levels. Toxic elements, namely Pb, Cd and As in the studied fish species were found to be higher than the values recommended for human seafood consumption. The study provides a comprehensive baseline report on trace element bioaccumulation in several marine organisms that will aid in developing effective conservation strategies of the highly biodiverse lagoon complex.

Keywords Bioaccumulation · Marine organisms · Metals · Fishes · Magdalena Bay · Mexico

Introduction

Marine systems are subjected to contamination that originate from toxic chemicals, plastics, organics, sediment inputs (i.e., industrial, agricultural, deforestation, sewage and domestic discharges), radioactivity and oil spills due to human-induced activities (Wilhelmsson et al. 2013). Subsequently, marine contamination alters the physical, chemical and biological characteristics of marine ecosystems potentially threatening the biota, being more sensitive. Among all the contaminants, metals released from

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natural and anthropogenic processes are considered to be the major toxicological threat due to their persistence, abilities of bioaccumulation and biomagnification, effects on biogeochemical recycling and for their various possible ecological risks (Zhou et al. 2007; Gao and Chen 2012; Gu et al. 2012; Jiménez-Ballesta et al. 2018).

Trace metals in marine organisms are classified as essential (Cu, Zn, Fe and Mn), which are lethal at high concentrations and toxic elements (Cd, Pb, As, Hg), where even minimal levels can be hazardous. Metals enter organisms either directly from surrounding waters via the respiratory and dermal organs or as food particles through the digestive tract from the underlying sediment bed (Oliveira Ribeiro et al. 2005). An estimated 30–50% reduction in species richness are caused by marine contaminants particularly, metals (Johnson and Roberts 2009). Bioaccumulation in marine food webs not only threatens the biodiversity directly, but can also affect human health and well-being, when commercial species are involved (Jiménez-Ballesta et al. 2017). Trophic transfer of elements along a food chain can result in an increase, decrease or no change in elemental concentrations from lower to upper components of the food web finding its route even up to humans (Luoma and Rainbow 2008). Therefore, studies on the trophic transfer of metals would determine the principal route of human beings exposed to chemical toxicants (Walton et al. 2010). Numerous studies on the bioaccumulation of trace elements in organisms have been conducted in recent years (Hui-Chen et al. 2011; Zhang et al. 2015; Yang-Guang et al. 2015; Jitar et al. 2015; Nel et al. 2015; Dias and Nayak 2016; Monferrán et al. 2016; Wang et al. 2018; Sankar et al. 2018; Bonsignore et al. 2018; Rajeshkumar and Li 2018). Understanding the distribution of metals in marine organisms is considered to be a crucial part of investigation as it specifies the health of an ecosystem (Jezierska and Witeska 2006). Therefore, the present study aims to evaluate the concentrations of trace metals (Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd, As and Hg) in several marine organisms collected from Magdalena Bay, which is considered to be the largest wetland ecosystem in Baja California Sur supporting the country's economy in terms of seafood production.

Materials and methods

Study area

Located in the southwestern coast (25°47′21″N; 112°18′18″W–24°15′40″N; 111°18′5″W) of the Baja California Peninsula (Fig. 1), Magdalena Bay is said to be the continent's most diversified breeding grounds (Bizarro 2008) that embraces organisms from the temperate waters of California to that of the tropical waters of mainland Mexico. The lagoon is separated from the Pacific Ocean by two islands (Santa Margarita and Magdalena) to the west, whereas the eastern side is fringed by mangrove wetlands (Sujitha et al. 2017). Geologically, the region is positioned in the supra-subduction zone (Metcalf and Shervais 2008) and phases of phosphate and ophiolite deposits are present in the lagoon. For its extensive size (area 565 km^2; Sánchez-Montante et al. 2007), pristine beauty and ecosystem dynamics, the region is described as the "Chesapeake of the Pacific" (Dedina 2000). The bay is influenced by the classic wind-driven coastal upwelling system resulting in high productivity most of the year. The considerable biodiversity of the area is well protected by its barrier islands, mangrove wetlands and kelp forests (Bird et al. 2003). More than 161 species of fish belonging to 120 genera and 61 families, four species of sea turtles, crustaceans, dolphins, gray whales and sea lions are found in this bay (Tena 2010). Species of commercial importance include sardines, shrimps, squids, red crabs and abalones. Previous studies have documented instances of mortalities in fish, shellfish, birds and marine mammals in Magdalena Bay in 1992 (Ochoa et al. 1997) which has prompted the need for an assessment of contaminants in this system that generates 1.6 million tons of fish products (CONAPESCA 2013).

Sample collection

A total of 52 marine organisms were sampled in October 2014 from Magdalena Bay that included fishes, crustaceans, mollusks, echinoderms and different organs (muscle, kidney and liver) of stranded bottlenose dolphin (*Tursiops truncatus*). Subsequently, the samples were taxonomically identified with the help of published literature and biometry of each species was also measured simultaneously. The

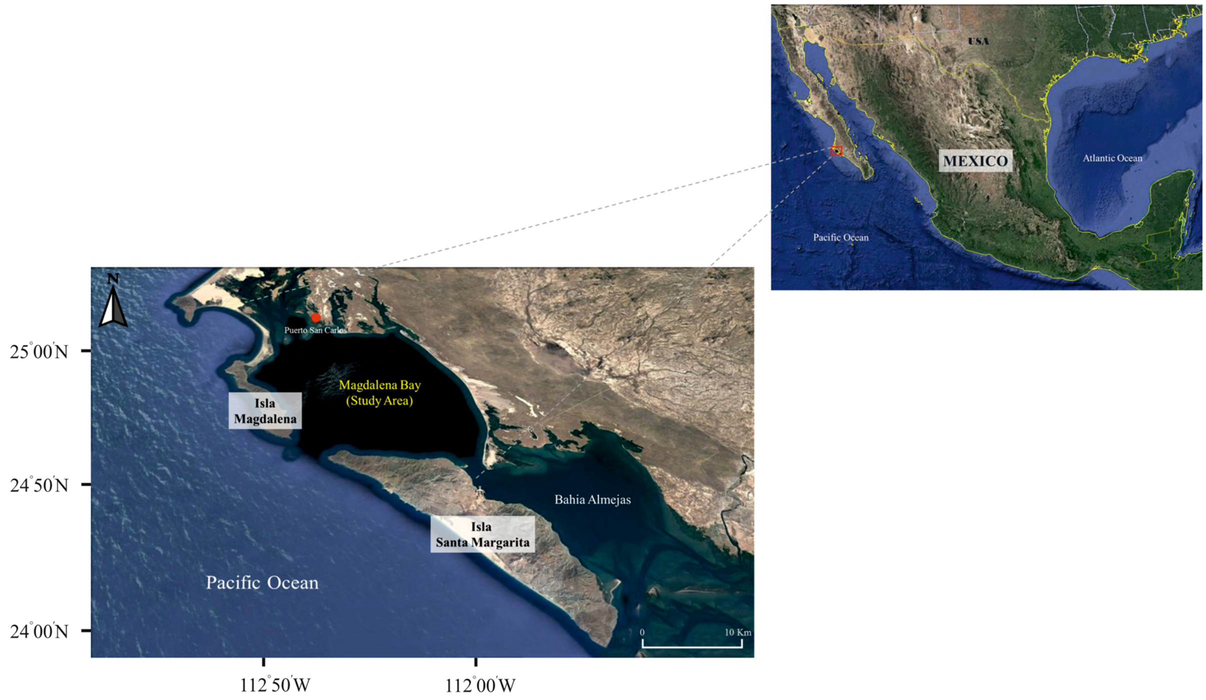


Fig. 1 Study area map, Magdalena Bay, Baja California Sur, Mexico

samples were washed in distilled water, dried at 50 °C and homogenized using an agate mortar for further analysis. Subsequently, 1 g of each dried powdered sample was digested using 3 ml HNO_3 + 2 ml HCl + 10 ml H_2O_2, and thereafter, the treated samples were heated in a hot plate at 60 °C for 4 h (Portman 1976; EPA 3010). The final solution was filtered and diluted up to 50 ml for the determination of Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd, As and Hg in AAS (*Perkin Elmer Model AAnalyst 100*). Estimation of Hg and As was carried out using the cold vapor technique and hydride generation, respectively. The detection limits of the instrument were (all values in $\mu g\ L^{-1}$): Fe (5), Mn (1.5), Cr (3), Cu (1.5), Ni (6), Co (9), Pb (15), Zn (1.5), Cd (0.8), As (0.03) and Hg (0.009). To maintain precision of the data, three replicate samples in fishes, mollusks, echinoderms and crustaceans, whereas five replicate samples for each individual organ of the dolphin (muscle, kidney and liver) were considered. A Certified Reference Material (CRM-TMF Lote. 1204706) for trace metals in fishes was tested after every five samples in order to ensure the accuracy of the equipment and the experimental procedure. The recovery percentages of metals for the entire analysis ranged from 88.71 to 101.2%.

Data analysis

Coefficient of condition

The coefficient of condition in fishes reflects the relative robustness or degree of the well-being of an individual fish which varies depending on the level of exposure to environmental conditions (Choongo et al. 2005). The coefficient factor depends on various aspects such as sex of the individual species, seasonal availability of feeds, water quality parameters and physiological characteristics (Khallaf et al. 2003). The coefficient of condition can be calculated using the following equation:

$$K = W \times 10^5 / L^3 \quad (Fulton 1904)$$

where K is the coefficient of condition, W is the weight of the fish in grams (g), and L is the standard length (from the tip of the upper lip to the median point of the caudal fin) in millimeters (Williams 2000). The calculated K value can be used to determine a fish's living condition and its stocking rate in a particular ecosystem.

Bioconcentration factor (BCF)

Bioconcentration is the process by which a chemical substance is absorbed by an organism from the ambient medium through its respiratory and dermal organs and the degree to which it occurs is defined by bioconcentration factor (BCF) (Arnot and Gobas 2006). BCF is calculated as: BCF = concentration of the chemical substance in the organism/concentration of the chemical substance in water.

Biota sediment accumulation factor (BSAF)

The biota sediment accumulation factor (BSAF) describes bioaccumulation of sediment-associated organic compounds or metals into tissues of ecological receptors (Burkhard 2009). This measurement reflects the efficiency of metal accumulation in an organism and permits the evaluation of the potential toxicity from sediment contaminants. BSAF is calculated by using the following formula (Thomann et al. 1995): BSAF = concentration of chemical substance in the organism/concentration of chemical substance in sediments.

Statistical analysis

Cluster analysis was performed for the entire dataset using Statistica version 12 to evaluate the discrepancies and similarities between measured metal levels in different marine organisms.

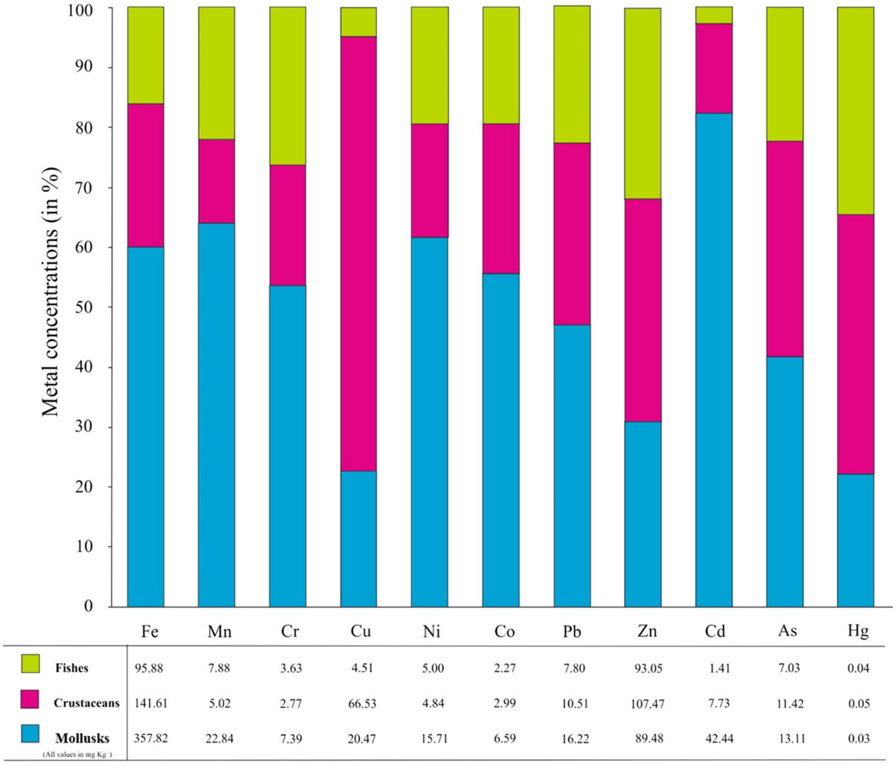
Results and discussion

Mollusks and echinoderms

The mean elemental concentrations of (Fig. 2) Echinoidea (sea urchins), Mollusks (*Murex* spp, *Mytilus edulis*), *Teuthida* (squids), *Asteroidea* (sea stars) presented an order of (values expressed in mg kg^{-1}): Fe (357.82) > Zn (89.48) > Cd (42.44) > Mn (22.8) > Cu (20.47) > Pb (16.22) > Ni (15.71) > As (13.11) > Cr (7.39) > Co (6.59) > Hg (0.03).

Mollusks due to their sedentary nature and high affinities to accumulate metals at higher concentrations than those found in the water column (Rainbow 2002) are considered to be potential bioindicators

Fig. 2 Average metal concentrations in fishes, crustaceans and mollusks collected from Magdalena Bay, Baja California Sur, Mexico



	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn	Cd	As	Hg
🟩 **Fishes**	95.88	7.88	3.63	4.51	5.00	2.27	7.80	93.05	1.41	7.03	0.04
🟥 **Crustaceans**	141.61	5.02	2.77	66.53	4.84	2.99	10.51	107.47	7.73	11.42	0.05
🟦 **Mollusks**	357.82	22.84	7.39	20.47	15.71	6.59	16.22	89.48	42.44	13.11	0.03

(All values in mg Kg^{-1})

(Silva et al. 2006; Maanan 2008). In general, high concentrations of Fe in mollusks and echinoderms are attributed to their cell types that demonstrate Fe histochemically in cytoplasmic inclusions; moreover, being rich in lysosomes, mollusks present high affinities to sequester or bind metals (Haas and Franz 2009). Extremely high levels of Fe in *Murex spp*. (537.58 mg kg^{-1}) are primarily sourced from the sediments (Cadena-Cárdenas et al. 2009), whereas in Echinoidea (456.40 mg kg^{-1}) it is due to their consumption of Fe-rich seaweeds and chlorophytes (Bielmyer et al. 2012). Elevated concentrations of Zn (89.48 mg kg^{-1}) in mollusks are due to its important role in various metabolic functions and metal-dependent enzymes (Craig and Overnell 2003). *Teuthida* presented high concentrations of Zn (79.21 mg kg^{-1}) and Cu (29.32 mg kg^{-1}) due to the storage of these metabolizable elements in the digestive gland of cephalopods (Penicaud et al. 2017). Enrichment of Cd (42.44 mg kg^{-1}) in mollusks and echinoderms is possibly from the local upwelling events (Lares et al. 2002) and cadmium-rich phosphorites. The potential sources of As include ship waste, harbor activities and anti-corrosive paints used on marine vessels from the nearby San Carlos Port and also from the naturally occurring arsenic-rich phosphate deposits (Shumilin et al. 2005; Leal-Acosta et al. 2010). The presence of Pb, Ni, Cr and Cu can be related to the regional geologic conditions (Gnandi and Tobschall 1999). Among the studied species, *Murex sp* with high concentrations of metals (914.08 mg kg^{-1}) can be regarded as a potential bioindicator in Magdalena Bay clearly stating the fact that uptake and accumulation in deposit feeders mostly correlate with bioavailability of metal concentrations in sediments (Gupta and Singh 2011).

Crustaceans

High accumulation of metals (Fig. 2) was observed in crabs (*Callinectes sapidus*, *Paguristes sp*): 465.79 mg kg^{-1}, lobsters (*Panulirus gracilis*, *Panulirus interruptus*): 375.98 mg kg^{-1} and shrimps (*Penaeus stylirostris, Penaeus californiensis*): 241.02 mg kg^{-1}. Hermit crabs (*Paguristes* spp.) exhibited the highest concentration of Fe (334.38 mg kg^{-1}) among the studied crustaceans due to their exposures to large amounts of iron oxides present in the sediments (Hacherl et al. 2001). High Zn levels observed in decapod crustaceans [198.06 mg kg^{-1} in *Panulirus interruptus* (California spiny lobster), 98.38 mg kg^{-1}in *Paguristes* spp (hermit crab) and 81.60 mg kg^{-1} in *Penaeus stylirostris* (brown shrimp)] are largely enzymatically bound zinc used for various biological functions (Eisler 2000). Cu concentrations in lobsters (90.24 mg kg^{-1}), shrimps (62.65 mg kg^{-1}) and crabs (46.71 mg kg^{-1}) are due to the presence of Cu in the respiratory pigment and its role in metabolic activities (Barwick and Maher 2003). Arsenic levels in the shrimp species ranged from (12.84 – 13.92 mg kg^{-1}) as they feed on marine algae and organic detritus often rich in organic arsenic (Neff 2002). *Penaeus stylirostris* (blue shrimp) presented high (254.70 mg kg^{-1}) concentrations of metals than *Penaeus californiensis* (227.33 mg kg^{-1}), as the former species thriving in shallow (0–27 m) muddy substrates possess high probability to accumulate contaminants rapidly. High levels (all values in mg kg^{-1}) of Zn (155.20), Fe (91.80) and Cu (90.24) in lobsters are probably due to the rapid accumulation of elements via gills (Szefer et al. 1990). However, both the lobster species [*Panulirus gracilis* (375.65 mg kg^{-1}) and *Panulirus interruptus* (376.16 mg kg^{-1})] presented similar patterns of metal accumulation.

Fishes

The average metal concentrations in the fish species (Fig. 2) were found to be (all values in mg kg^{-1}): Fe (95.88) > Zn (93.05) > Mn (7.88) > Pb (7.80) > As (7.03) > Ni (5.00) > Cu (4.50) > Cr (3.63) > Co (2.27) > Cd (1.41) > Hg (0.04). The results clearly indicate the fact that species individuality, trophic position, habitat, feeding characteristics, absorption rate and metal phase (particulate or dissolved) play a vital role in the bioaccumulation of trace elements in different fish species (Asuquo et al. 2004). Fe (792.99 mg kg^{-1}) and Cr (22.51 mg kg^{-1}) levels found in *Mugil curema* can be related to its carnivorous feeding habit and the local geological conditions rich in ophiolites (Rodríguez-Meza et al. 2008). Moreover, Fe is considered to be an essential element for the transportation and functioning of blood (Voigt et al. 2015). Species inhabiting the demersal and benthopelagic zones contained high concentrations of Mn [(all values in mg kg^{-1}) *Achirus mazatlanus*: 43.51; *Mugil curema*: 21.68; *Balistes Polylepis*: 21.16;

Table 1 Comparison of metal concentrations in the studied fish species with that of the maximum permitted values worldwide

Elements	Present study	WHO (1985)	FEPA (2003)	FAO (1983)	EU (2001)	Mexican values (1993)[a]
Fe	89.99	–	–	–	0.5	–
Mn	9.08	0.5	0.5	–	–	–
Cr	6.70	0.15	0.15	–	1	–
Cu	3.94	3	1.3	30	1	–
Ni	8.44	0.6	0.5	–	1.5	–
Co	5.24	–	–	–	–	–
Pb	11.52	2	2	0.5	–	1.0
Zn	94.27	10–75	75	30	–	–
Cd	1.69	–	–	0.5	–	0.5
As	14.42	–	–	–	1	–
Hg	0.49	–	–	–	1	1.0

All values are expressed in mg kg^{-1} (dry wt.)

WHO World Health Organization, *FEPA* Federal Environmental Protection Agency, *FAO* Food and Agriculture Organization of the United Nations, *EU* European Union

[a] Norma Oficial Mexicana NOM-031-SSA1-1993

Menticirrhus panamensis: 20.19] possibly derived from the carbonates, sulfides, oxides and phosphate deposits that are rich in Mn (Nayak 2015). High average Zn levels in fishes (93.05 mg kg^{-1}) are due to the biophilic property of the element (Moiseenko and Kudryavtseva 2000) and high physiological demand. High concentration of As (30.84 mg kg^{-1}) is probably sourced from the phosphorite-enriched sedimentary unit and intense upwelling in the study region (Farías et al. 2002; Shumilin et al. 2005).

Metal concentrations in the studied fish species (avg. of all samples in dry wt.) were also compared with the maximum permissible limits for human consumption put forth by various organizations (Table 1). Dissimilarities observed in the metal concentrations of individual species from the same environment can be related to the differences in their physiological tolerance, body reaction, feeding habitats, absorption rates and regulatory mechanisms (Rozon-Ramilo et al. 2011; Monikh et al. 2013; El-Sadaawy et al. 2013). In general, higher mean elemental concentrations of Fe, Zn, Mn, Pb and As reflect the geological and environmental setting of Magdalena Bay. However, essential elements like Fe, Mn, Zn, Cu, Cr and Ni are vital to the functioning of the metabolic and physiological processes, whereas nonessential elements like Cd, As, Pb and Hg are the most ecologically perilous elements, because they can be substituted for metabolic processes resulting in physiological disturbances (Brzoska and Moniuszko-Jakoniuk 2001).

Dolphin

Trace metal concentrations in the muscle, kidney and liver of dolphin species are presented in (Fig. 3). On an average, hepatic tissues presented higher concentrations of metals (94.40 mg kg^{-1}) compared to the renal (69.58 mg kg^{-1}) and muscular tissues (45.17 mg kg^{-1}). High levels of metals observed in the hepatic tissues are due to their increased metabolic activities and copious lipid contents (Last and Stevens 2009) in contrast, less concentrations of metals in muscles are attributed to low binding affinities of binding proteins in the muscle (Storelli et al. 2011). High levels of Fe, Mn, Cu and Hg were observed in liver; Cd and As in kidney; and Zn, Cr, Ni, Co, Pb in muscle. These differences are linked to the selectivity and affinity of each organ for the accumulation of different metals (Monteiro-Neto et al. 2003).

The presence of Fe (700.7 mg kg^{-1}) and Mn (10.81 mg kg^{-1}) indicates the essentiality of these elements that are mainly regulated by the organism (Roditi-Elasar et al. 2003). Cu levels (18.51 mg kg^{-1}) observed in the liver are related to the organ's role in detoxifying and excreting harmful substances

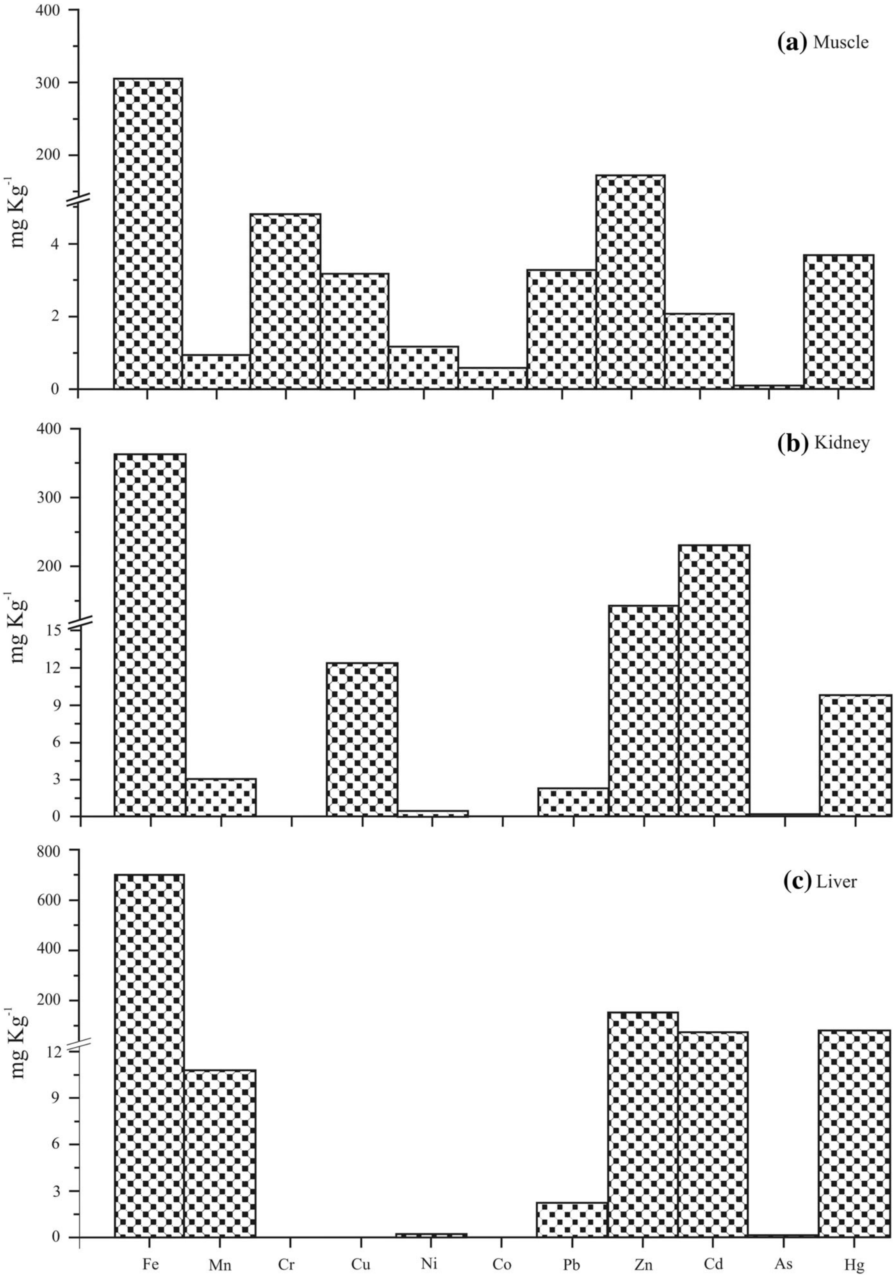


Fig. 3 Distribution of metals in muscle, kidney and liver tissues of dolphin collected from Magdalena Bay, Baja California Sur, Mexico

(Frodello et al. 2002); in addition, the bioaccumulation of Cu increases with increasing trophic position as many sentinel organisms fail to excrete Cu efficiently (Bilandžić et al. 2016). High hepatic Hg levels (77.94 mg kg^{-1}) are attributed to the fact that liver proves to be an active site for demethylation process (Hui-Chen et al. 2011). Elevated levels of hepatic Hg also suggest higher rate of assimilation than excretion and reduced detoxification efficiency (García-Alvarez et al. 2015). However, arsenic concentrations were found to be low (avg: 0.15 mg kg^{-1}), due to the fact that As concentrations in marine mammals rarely exceed 1.0 mg kg^{-1} in any tissue (Thompson 1990). Cd values were found to be high in the kidneys (230.09 mg kg^{-1}) and liver (74.04 mg kg^{-1}), reflecting the filtering function of the renal organs and the high dietary fraction of cephalopods, as dolphins are commonly called Cd accumulators (Bustamente et al.

Table 2 Mean bioconcentration factor (BCF) and biota sediment accumulation factor (BSAF) values of marine organisms collected from Magdalena Bay, Baja California Sur, Mexico

	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn	Cd	As	Hg
Metals in water (mg/L)[a]	0.0091	0.0003	0.0089	0.0139	0.1923	0.1239	–	0.0045	0.0167	0.2262	–
BCF											
Fishes	10,391	25,790	398	322	25	18	–	20,412	83	81	–
Crustaceans	15,562	16,717	311	4786	25	24	–	23,882	463	50	–
Mollusks	48,949	83,891	1037	1221	119	75	–	23,152	2603	46	–
Metals in sediments (mg/Kg)[a]	9744.79	123.20	227.21	3.98	16.13	8.57	10.23	14.12	1.57	3.25	0.01
BSAF											
Fishes	0.01	0.06	0.02	1.17	0.35	0.29	0.80	6.62	0.95	2.16	3.46
Crustaceans	0.01	0.04	0.04	16.72	0.30	0.35	1.03	7.62	3.00	3.51	5.04
Mollusks	0.04	0.19	0.03	5.14	1.22	0.77	1.58	6.35	27.03	4.04	1.55

[a] SIP project report: 20140191 and 20150324

1998). Similar concentrations of Zn observed in muscle (172.24 mg kg^{-1}), liver (153.12 mg kg^{-1}) and kidney (142.50 mg kg^{-1}) were observed to be consistent with other studies, indicating that cetaceans present extremely high levels of Zn, that can be up to ten or hundred times higher than other elements (Yang et al. 2002; Stavros et al. 2007) as it plays a major role in photo-oxidation from solar radiation, tumor progression, skin inflammation and wound healing (Leccia et al. 1999). Less Pb values (2.60 mg kg^{-1}) are probably due to its tendency to accumulate in the bone tissues (Becker 2000) that follows a metabolic path similar to calcium.

Discussion

Coefficient of condition

Nearly 85% of the fishes in the study region presented K values > 1, indicating a healthy ecosystem. Among the analyzed fish species (Suppl. Table 1), Pacific spadefish (*Chaetodipterus zonatus*) presented a K value of 5.78 indicating isometric growth due to the above average habitual conditions predominant in the region (Ayode 2011). However, Mexican barred snapper (*Hoplopagrus guentherii*) recorded a value of 0.12 suggesting unsuitable ecological conditions (Nehemia et al. 2012). In general, fishes of Magdalena Bay presented a mean K value of 1.33 representing well-proportioned growth under favorable environmental and biological attributes (Datta et al. 2013).

Bioconcentration factor (BCF)

BCF values presented an order of (a) fishes: Mn > Zn > Fe > Cr > Cu > Cd > As > Ni > Co, (b) crustaceans: Zn > Mn > Fe > Cu > Cd > Cr > As > Ni > Co and (c) mollusks: Mn > Fe > Zn > Cd > Cu > Cr > Ni > As > Co. In general, BCF values > 1000 (Table 2) for Mn, Fe, Zn, Cd and Cu suggest slow accumulation, potentiality for chronic effects and accretion in the food chain (De-Forest et al. 2007; Kwok et al. 2014). High mean BCF values for Mn (37,889) are possibly due to the upward diagenetic remobilization and sediment resuspension processes that highly influence Mn mobilization from sediments to the overlying waters (Gueiros et al. 2003).

In the case of dolphins, highest BCF values were presented by the hepatic tissues and the general trend of metal accumulation was Fe > Mn > Zn > Cd > Cu > Ni > As > Cr > Co. The differences in BCF values can be related to several characteristics of the species, namely age, sex, body size, trophic position and the exposure time to contaminants (Kojadinovic et al. 2007).

Biota sediment accumulation factor (BSAF)

BSAF values (Table 2) presented an order of (a) fishes: Zn > Hg > As > Cu > Cd > Pb > Ni > Co > Mn > Cr > Fe; (b) crustaceans: Cu > Zn > Hg > As > Cd > Pb > Co > Ni > Mn > Fe > Cr; (c) mollusks: Cd > Cu > Zn > As > Hg > Pb >

Ni > Co > Mn > Fe > Cr. According to Dallinger (1993), fishes can be classified based on their BSAF values as macro-concentrator (BSAF > 2), micro-concentrator (1 < BSAF < 2) and deconcentrators (BSAF < 1). Henceforth, the studied fish species are categorized as micro-concentrators (Avg. BSAF: 1.42) of metals from the sediments. High BSAF values for Cu and Zn by the crustaceans and mollusks are due to high metabolic rates of small organisms, and moreover, metallothionein proteins in aquatic invertebrates play an important role in the homeostasis of essential metals like Cu and Zn (Sarkar et al. 2006). High BSAF value for Cd in mollusks is due to the association of Cd with exchangeable carbonates and organic phases that are highly bioavailable from the sediment beds. Likewise, hepatic Hg values in dolphin presented high BSAF values (7794) clearly indicating the biomagnifying property of Hg, particularly in the liver due to its role in detoxification process (Wagemann et al. 2000).

Statistical analysis

Cluster analysis was performed to evaluate the association of trace elements (Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd, As, Hg) in different marine organisms (Fig. 4a–d). Fe, which is regarded as the second most common crustal metal in the environment, was also observed to be the controlling element in all the obtained dendrograms, for its highly significant role in respiratory pigments such as hemoglobin and myoglobin, tissue oxidation, oxygen and electron transfer within the body (Bury et al. 2001). The independent behavior of Zn in the fish species (Fig. 4a) can be attributed to its various functions, including metabolism of nucleic acids, proteins, lipids and carbohydrates (Murakami and Hirano 2008); additionally, Zn

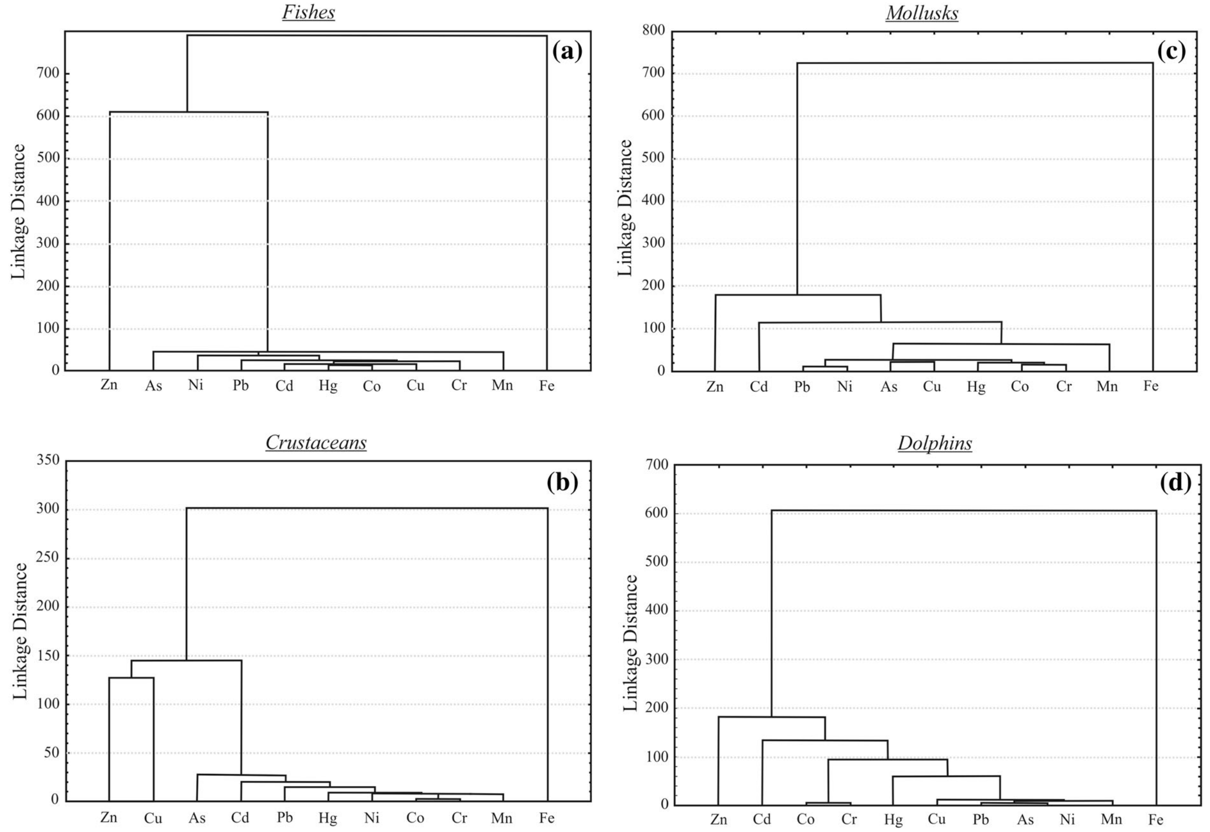


Fig. 4 **a–d** Dendrograms obtained for metals in fishes, crustaceans, mollusks and dolphin (muscle, liver and kidney) from Magdalena Bay, Baja California Sur, Mexico

also regulates the uptake and diminution rates of other elements sequestered for the organism's metabolism needs (Marcovecchio and Moreno 1993).

In crustaceans (Fig. 4b), the interlinkage of Zn and Cu is due to their similar biological requirements as they possess a Cu containing protein (hemocyanin) that functions as an oxygen transport molecule (Barwick and Maher 2003). The interlinkage of Cd and Zn in bivalve mollusks (Fig. 4c) indicates their similar physicochemical properties and binding empathies to the same proteins in the tissues (Brzoska and Moniuszko-Jakoniuk 2001). In mollusks, the relationship between Mn and the other elements is due to its role in coordinating the binding sites in mitochondria (Kendrick et al. 1992). The relationship of As, Ni, Pb, Hg, Cd, Co, Cu, Cr and Mn reflects their analogous geologic source and similar bioaccumulation mechanism. The dominance of Zn after Fe in majority of the biological organisms is rightly inferred for its role in metabolic activities and high bioregulation. Variations observed in the elemental associations of metals are also due to the functional differences and distinct tissue metabolism posed by individual species (Storelli et al. 2011).

Trophic transfer and accumulation

Studies on the trophic accumulation of metals to determine elemental biomagnification patterns are of utmost importance considering the potential risk to human health. The most important factors regulating the transfer and accumulation of metals by individual species along the trophic levels include the efficiencies of assimilation, accumulation and excretion rates (Soto-Jimenez 2011). Biological and environmental conditions also play a vital role in determining elemental speciation and concentration. Toxicants that accumulate in organs and tissues of the organism are normally higher than those in the organism's habitat; moreover, some elements can biomagnify in the trophic food chain resulting in ecological imbalances and adverse physiological effects for top predators including humans (Jara-Marini et al. 2009; Borrell et al. 2016). It is important to identify the trophic routes and bioaccumulation trends of heavy metals in marine species. Thus, robust analyses must be carried out in order to assess the trophic accumulation of metals. In the present study, an attempt has been made to understand the accumulation of metals in the studied marine species of different trophic levels.

The different accumulation patterns of metals based on the trophic positions of each organism can be presented in the following order (Fig. 5): (1) Dolphin: Fe > Zn > Cd > Hg > Cu > Mn > Cr > Pb > Ni > Co > As; (2) Fishes: Fe > Zn > Mn > Pb > As > Ni > Cu > Cr > Co > Cd > Hg; (3) Crustaceans: Fe > Zn > Cu > As > Pb >

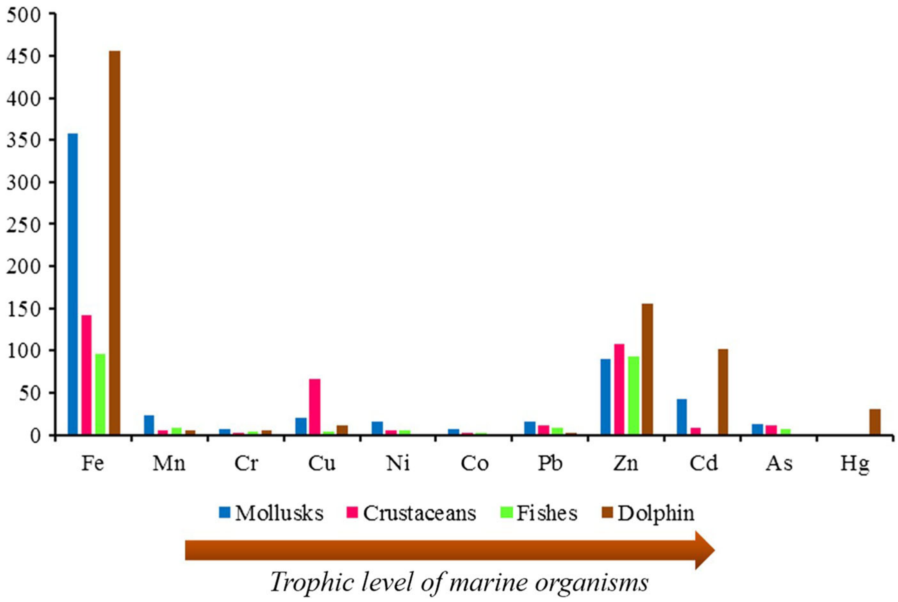


Fig. 5 Trophic accumulation of metals in marine organisms collected from Magdalena Bay, Baja California Sur, Mexico

Cd > Mn > Ni > Co > Cr > Hg; (4) Mollusks and echinoderms: Fe > Zn > Cd > Mn > Cu > Pb > Ni > As > Cr>Co > Hg.

In the present study, Mn, Cr, Cu, Ni, Co, As and Pb exhibited no trend of trophic accumulation, whereas nonessential elements like Hg and Cd displayed a well-defined increasing trend along the trophic positions. The trophic accumulation of Cd [(all mean values in mg kg^{-1}) mollusks and echinoderms: 42.44; crustaceans: 7.73, fishes: 1.41, dolphin: 102.29] is ascribed to the fact that Cd normally accumulates as an inert storage molecule with long half-lives (Rabinowitz 1991). Furthermore, dolphins can also accumulate Cd from cephalopods that are known as Cd accumulators (Bustamente et al. 1998). The increasing trophic accumulation of Hg observed in the present study [(all mean values in mg kg^{-1}) mollusks: 0.03; crustaceans: 0.05; fishes: 0.04; dolphin: 30.49] is attributed to its slow depuration rate and lower detoxification ability of marine predators (Gray 2002). Arsenic levels were found to be decreasing along the trophic levels (all mean values expressed in mg kg^{-1}), mollusks: 13.11, crustaceans: 11.42, fishes: 7.03, dolphin: 0.15), due to the fact that As does not appear to biomagnify between trophic levels and at the same time they are rapidly excreted (Campbell et al. 2005).

Conclusion

The present study provides an integrated dataset of metal accumulation in different marine organisms that can be a potential hazard for the top consumers including humans. High values of Fe, Zn, Mn, Pb and As suggest that, in addition to anthropogenic stresses, natural factors, namely local geology, lithological characteristics and hydrothermal processes, also play a significant role in metal accumulation. Calculated BCF and BSAF values reflected the bioavailability and toxicity of each metal in Magdalena Bay. In general, bioaccumulation of metals in the studied marine organisms presented an order of (all mean values in mg kg^{-1}): Fe (263.01) > Zn (111.49) > Cd (38.47) > Cu (25.72) > Mn (10.17) > Pb (9.28) > As (7.93) > Hg (7.65) > Ni (6.53) > Cr (4.65) > Co (3.10). Extremely high levels of toxic metals such as Cd, Pb and As, when compared to the permissible limits for human consumption in the studied fish species, call for immediate precautionary measures, considering the important role of fisheries in this part of the country. Moreover, high concentrations of metals in the commercial species like *Mugil curema* and *Penaeus californiensis* (brown shrimp) demand instant remedies as bioaccumulation of heavy metals in seafood has caused major heath concern in humans worldwide. Henceforth, the present study fulfills the recent trend of comprehensive assessment of an ecosystem by providing baseline data in bioaccumulation of metals in different marine organisms.

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Compliance with ethical standards

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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