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RESEARCH ARTICLE

Trace metals in target tissues and stomach contents of the top predator sailfish *Istiophorus platypterus* from the Eastern Pacific: concentrations and contrasting behavior of biomagnification

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Abstract Cadmium, lead, copper, and zinc were analyzed in the dorsal muscle, liver, gonad, and stomach contents of 67 sailfish, *Istiophorus platypterus*, from the Eastern Pacific. Muscle exhibited the following pattern (μg/g wet weight): Zn (15.05 ± 1.24) > Cu (0.461 ± 0.026) > Cd (0.434 ± 0.099) > Pb (0.025 ± 0.001); liver Zn (119.1 ± 7.6) > Cd (95.1 ± 11.0) > Cu (39.7 ± 2.6) > Pb (0.047 ± 0.004); and gonad Zn (96.8 ± 7.8) > Cd (2.16 ± 0.38) > Cu (2.08 ± 0.14) > Pb (0.033 ± 0.003). Significant ($p < 0.05$) correlations were observed between elements, length, and weight. *I. platypterus* feed mainly on fishes and cephalopods with variable concentrations (μg/g wet weight) of Cd (0.081–11.41), Pb (0.002–0.057), Cu (0.204–4.35), and Zn (3.23–86.6). Of the four analyzed elements, only Pb was biomagnified (BMF = 1.85). According to the regulatory limits, muscle exhibited Cd concentrations higher than the Official Mexican Standard, WHO, FDA (28 % of samples), and the European Union (40 %) regulations.

Keywords Cadmium · Lead · Copper · Zinc · *Istiophorus platypterus* · Gulf of California · Eastern Pacific

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Introduction

Metals from natural and anthropogenic sources are present in aquatic ecosystems (Montalvo et al., 2014), so it is feasible that organisms absorb them via the dermal (body surface), food, and respiratory tissue such as gills or mouth; after absorption, metals are transported through the blood and accumulated in different tissues or organs (Rand 1995; Newman and Unger 2003). As a consequence, metals may be transferred through the food web resulting in increased concentrations among trophic levels; in other words, biomagnification might occur (Gray 2002). Eventually, a risk to the health of marine life would be induced (Baby et al., 2010).

The predatory sailfish, *Istiophorus platypterus*, located at the top of the marine food web, is particularly exposed to relatively high concentrations of metals (Soto-Jiménez et al., 2010; Bergés-Tiznado et al., 2015). Metal exposition can be influenced by the migratory pattern of *I. platypterus* that enhances contact with the waters of different places because of periodic latitudinal massive movements parallel to the coast with transboundary crossing ranging from 12 to 20 days in each place (Prince et al., 2006; Macías-Zamora et al., 2011). *I. platypterus* is considered as a single stock population in the Eastern Pacific Ocean (Squire 1974; McDowell 2002; Hinton

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and Maunder 2013; Lu et al., 2015), distributed from Peru to Mexico (Nakamura, 1985). In Mexico, one of the centers of abundance of sailfish is the southeastern Gulf of California (Ortega-García et al., 2008), which have optimal temperatures that favor the reproduction and feeding of this fish (Santana-Hernández et al., 2009; Ramírez-Pérez et al., 2011). This predator has a high metabolic rate and tends to intake a large variety of fish, crustaceans, and cephalopods (Fischer et al., 1995; Idrisi et al., 2002). Therefore, the uptake metals can be directly influenced by the surrounding water and/or consumed organisms (food) (Bryan 1979; Authman et al., 2015).

Cadmium, Pb, Cu, and Zn are considered as relevant metallic pollutants of the aquatic environment because they may interfere with metabolic activities in freshwater, marine, and estuarine biota; however, evidence of biomagnification of these elements is not consistent for all trophic webs (Szefer 1991; Gray 2002; Ruelas-Inzunza and Páez-Osuna 2008). Nevertheless, there are food chains where biomagnification of Cd, Pb, Cu, and Zn have been frequently reported; the trophic relation of bivalves, herbivorous gastropods, barnacles, and carnivorous gastropods is an example (Cardwell et al., 2013). The aim of the present study is to establish the levels of Cd, Pb, Cu, and Zn in the dorsal muscle, liver, gonad, and stomach contents of sailfish (*I. platypterus*) from the southeastern Gulf of California. Also, the biomagnification factor (BMF) for such elements using the muscle and prey species found in the stomach contents was calculated. The levels of Cd, Pb, Cu, and Zn in edible muscle of sailfish were compared with the Mexican and international permissible limits for human consumption. The regulatory limit of metals in fish used for comparison in this study were the Official Mexican Standard (0.5 μg/g ww for Cd and Pb; SEGOB 2011), the European Union (EU) (0.3 μg/g ww for Cd and Pb; CREC 2006), the World Health Organization (WHO) (0.5 μg/g ww for Cd and 0.3 μg/g ww for Pb; FAO/WHO 1972), the US Food and Drug Administration (FDA) (0.5 μg/g ww for Cd and 1.3 μg/g ww for Pb; FDA 1993a, 1993b), Australia (10 μg/g ww for Cu and 150 μg/g ww for Zn; Nauen 1983), India (10 μg/g ww for Cu and 50 μg/g ww for Zn; Nauen 1983), and New Zealand (30 μg/g ww for Cu and 40 μg/g ww for Zn; Nauen 1983).

Materials and methods

Sampling

The samples were obtained during three sport fishing tournaments off Mazatlan (semicircle area adjacent to Mazatlan port, Fig. 1), Sinaloa, Mexico, in November 2011, 2012, and 2013. A total of 67 sailfish were collected and dissected, and the lower jaw fork length (LJFL) and total weight were determined. Approximately 50–75 g of edible muscle was sampled from the dorsal region of each specimen. The liver, gonad, and stomach were also removed and subsequently analyzed. In the case of gonad, only 63 samples were available; the sex was determined by visual inspection of the gonad morphology (Shimose et al., 2012). Samples were processed in the field using a mobile laboratory.

Index of relative importance

The muscle, liver, gonad, and stomach contents were placed in separate plastic bags and kept in coolers during transport to the laboratory. Prey items in the stomach contents were identified according to the keys of Clothier (1950), Fitch and Brownell (1968), Wolff (1984), Allen and Robertson (1994), Fischer et al. (1995), and Thomson et al. (2000); the index of relative importance (IRI) was calculated according to Pinkas et al. (1971) and Cortés (1999): IRI = $(\%N + \%W) \times (\%F)$, where $\%N$ is the number of individuals of each species in the stomachs, expressed in percentage of total prey items in the stomach contents; $\%W$ is the gravimetric method based on the weight of each prey species; this is referred to as percentage of total weight of all prey items in the stomach contents; $\%F$ is the frequency of occurrence method; it reflects the frequency of each food item, i.e., presence or absence, in all stomachs that contained food.

Analytical procedure

The tissue samples and the prey from the stomach contents were separately homogenized and freeze-dried for 72 h (−49 °C and 133×10^{-3} mbar) and then pulverized in a semi-automatic agate mortar and by hand. Aliquots of samples (0.250 ± 0.003 g of dry tissue) were digested in Teflon vials with caps (Savillex) with 5 mL of concentrated HNO_3 (Ultrapure ≥65 %) at 120 °C for 3 h. The digested samples were diluted with purified milli-Q water to a final volume of 20 mL (Bergés-Tiznado et al., 2015). All samples were analyzed in duplicate. Blanks and a standard reference material, DOLT-4 (dogfish liver; NRC-CNRC 2008), were digested (one in each batch of 25 samples) using the same procedure to control for accuracy and precision.

Trace metals were quantified by atomic absorption spectrophotometry (Varian SpectrAA220): Cd, Pb, and Cu (graphite furnace), and Zn (flame). Elemental concentrations were expressed as microgram/gram on a wet weight basis (ww). Measured concentrations in reference material were within certified intervals for all elements: percentage recoveries were 99.6 ± 1.2 for Cd, 96.6 ± 6.2 for Pb, 99.0 ± 1.0 for Cu, and 98.5 ± 0.9 for Zn. The coefficients of variation were 1.1 % for Cd, 6.2 % for Pb, 1.1 % for Cu, and 0.7 % for Zn. Limits of detection (μg/g) of Cd, Pb, Cu, and Zn were 0.001, 0.002, 0.009, and 0.01, respectively.

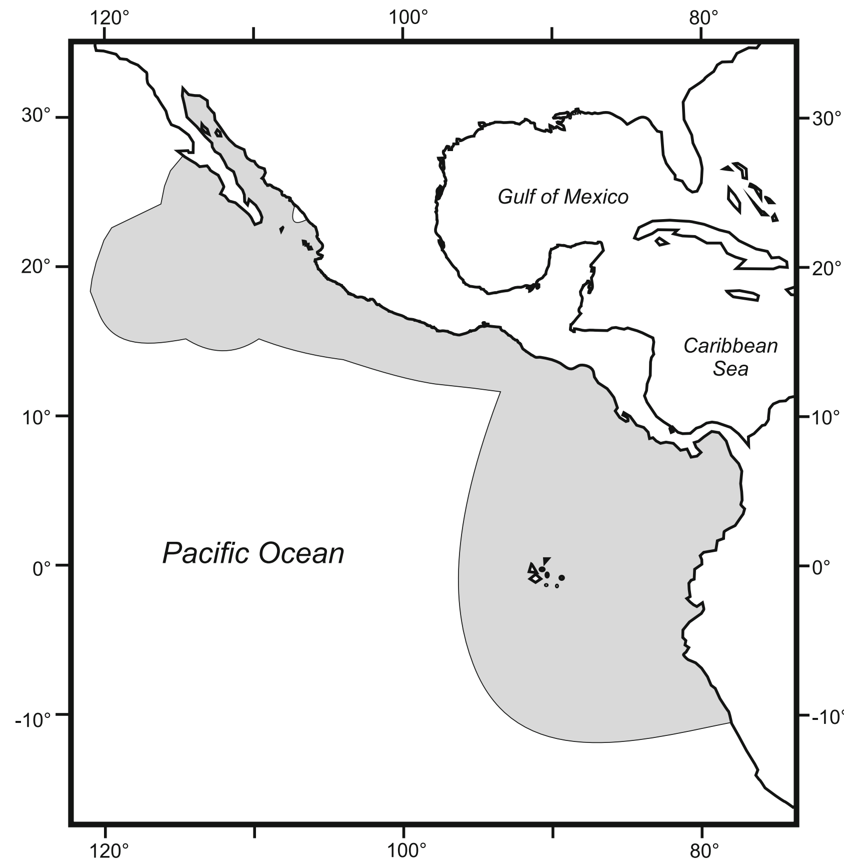

Fig. 1 Distribution of *I. platypterus* in the Eastern Tropical Pacific; the *contour line of the Pacific* indicates limits of movements of the species in this region (modified from Fisher et al., 1995; Prince et al., 2006); the *semicircle* represents the sampling location adjacent to Mazatlan (Mexico)

Biomagnification factors

The BMF was calculated according to Gray (2002) and as used by Lavoie et al. (2010) and Ruelas-Inzunza et al. (2014): BMF = concentration in predator/concentration in prey; if the BMF > 1, the element is biomagnified.

Statistical analysis

Metal datasets were statistically compared with a Kruskal-Wallis non-parametric ANOVA; the influence of sex was compared with a Mann-Whitney *U* test; Spearman rank correlations (R) were used to determine associations among metal levels, length, and weight; significance level used in these analyzes was $p < 0.05$ (Montgomery 2004; Zar 2010). To determine whether there were differences in diet between sexes, similarity was analyzed using a permutation randomized method in a Bray-Curtis dissimilarity matrix (ANOSIM, in Primer 6.1.7). The results of this analysis show an overall R_{ANOSIM} ranging between 0 and 1 and global p value of significance (in percentage); if R_{ANOSIM} is near zero, it indicates that the similarities within each group and between groups do not have any separation and if $R_{\mathrm{ANOSIM}} = 1$ or near, it indicates a high separation within each group and between groups (Clarke and Warwick 2001).

Results and discussion

Biometry

Biometric data of the studied sailfishes (Table 1) indicated that the organisms were mature adults, because they were in the estimated size of sexual maturity (145 to 235 cm) (Nakamura, 1985; Fisher et al., 1995); some studies indicated that *I. platypterus* presents the first sexual maturity at a size of 150.2 to 165 cm or even at smaller sizes of 123.6 cm (Eldridge and Wares 1974; Froese and Pauly 2010; Cerdenares-Ladrón 2011).

Trace element concentrations

Concentrations of Cd, Pb, Cu, and Zn (μg/g ww) in the liver, gonad, and muscle of sailfish, *I. platypterus*, are presented in Table 2. In general, the measured metals accumulated mainly in the liver followed by the gonad and finally in the muscle. In the liver and gonad, the sequence of the tested elements was Zn > Cd > Cu > Pb, while, in the muscle Zn and Cu levels were higher than non-essential metals (Zn > Cu > Cd > Pb). Differences in the accumulation of the elements in tissues are mainly based on the biochemical characteristics and the biological function of each one. The liver, gonad, and muscle

Table 1 Biometric data of *I. platypterus* sampled

	Sample	LJFL (cm)		Weight (kg)	
	n	Mean ± SE	Min-max	Mean ± SE	Min-max
Male	29	191.3 ± 2.6	170.0–240.0	25.8 ± 0.7	19.1–33.3
Female	38	193.8 ± 2.3	163.0–228.0	26.8 ± 0.8	19.8–37.4
Total	67	192.7 ± 1.7	163.0–240.0	26.4 ± 0.5	19.1–37.4

LJFL lower jaw fork length, *SE* standard error, *Min-max* minimum-maximum

contain sulfhydryl (−SH), carboxyl (−COOH), and amino ($-NH_2$) groups that have affinity for diverse metals; this affinity facilitates the binding and retention of elements (Espina and Vanegas 2005). Besides, the liver is involved in the metabolism of all substances that come through the blood (Torres et al., 2010), i.e., it is related to uptake, storage, detoxification, and elimination of exogenous metals (Liu et al., 2014). The liver also participates in the synthesis of metallothioneins (Overnell and Coombs 1979); these proteins regulate the presence of Cu and Zn and play a protective role against essential and non-essential metals (Roesijadi 1992; Viarengo et al. 2000; Park et al., 2001; Mieiro et al., 2011). In vertebrates, and particularly in fish, metal detoxification processes depends mainly on metal binding to metallothioneins (Amiard et al., 2006). These proteins of low molecular weight are rich in cysteine (thiol (−SH) group) and have high affinities for the Cd and Zn ions and other ions such as Cu, Hg, and Ag (Kojima et al., 1976; Klaassen et al., 1999). This high affinity was reflected in this study because the liver mainly bioaccumulated Zn followed by Cd (Table 2). In the black marlin, *Istiompax indica*, the liver presented the same order of metal bioaccumulation Zn > Cd > Cu > Pb (Mackay et al., 1975).

The gonad was the second tissue that showed greater bioaccumulation of metals. The gonad presents an important metabolic activity, and they can regulate the synthesis of metallothioneins, which can be induced by the presence of metals and hormones (Olsson et al., 1990; Viarengo et al., 2000; Křížková et al., 2007). In the available literature, there is no information on the accumulation of Cd, Pb, Cu, and Zn in the gonad of *I. platypterus*, nor any species of the family Istiophoridae or other billfish (Table 3). However, it is known that sailfish (*I. platypterus*) migrates to the Baja California Peninsula in the summer and autumn during their reproductive period (Ramírez-Pérez et al., 2011). During the spawning period, steroids induce

Table 2 Mean ± SE (Min-max) concentrations of Cd, Pb, Cu, and Zn (μg/g ww) in the tissues of sailfish *I. platypterus*

Tissue	Number	Cd	Pb	Cu	Zn
			Muscle		
Male	29	0.588 ± 0.210^a	0.026 ± 0.002^a	0.485 ± 0.043^a	14.59 ± 1.94^a
		(0.039–6.135)	(0.015–0.050)	(0.250–1.406)	(6.03–61.36)
Female	38	0.316 ± 0.066^a	0.025 ± 0.001^a	0.443 ± 0.033^a	15.40 ± 1.63^a
		(0.018–1.984)	(0.008–0.047)	(0.209–1.409)	(6.02–67.66)
Total	67	0.434 ± 0.099^A	0.025 ± 0.001^A	0.461 ± 0.026^A	15.05 ± 1.24^A
		(0.018–6.135)	(0.008–0.050)	(0.209–1.409)	(6.02–67.66)
			Liver		
Male	29	98.7 ± 14.9^a	0.053 ± 0.008^a	31.9 ± 3.0^a	112.5 ± 11.5^a
		(16.5–349.7)	(0.022–0.255)	(15.3–84.2)	(61.9–329.0)
Female	38	92.3 ± 15.9^a	0.043 ± 0.003^a	45.6 ± 3.8^a	124.1 ± 10.3^a
		(11.3–473.7)	(0.021–0.095)	(11.7–109.2)	(58.8–345.9)
Total	67	95.1 ± 11.0^B	0.047 ± 0.004^B	39.7 ± 2.6^B	119.1 ± 7.6^B
		(11.3–473.7)	(0.021–0.255)	(11.7–109.2)	(58.8–345.9)
			Gonad		
Male	25	2.65 ± 0.49^a	0.035 ± 0.005^a	1.43 ± 0.14^a	40.1 ± 6.1^a
		(0.022–18.6)	(0.014–0.165)	(0.57–3.17)	(15.9–137.3)
Female	38	1.41 ± 0.31^a	0.032 ± 0.002^a	2.50 ± 0.19^b	134.1 ± 8.2^b
		(0.016–10.3)	(0.018–0.084)	(0.46–6.12)	(18.6–201.1)
Total	63	2.16 ± 0.38^C	0.033 ± 0.003^C	2.08 ± 0.14^C	96.8 ± 7.8^B
		(0.016–18.6)	(0.014–0.165)	(0.46–6.12)	(15.9–201.1)

Different lowercase superscript letter indicates significantly different ($p < 0.05$) mean concentrations between sexes for the same tissue and metal; different capital superscript letters indicate significantly different ($p < 0.05$) mean concentrations between tissues for the same metal

SE standard error

Table 3 Cd, Pb, Cu, and Zn concentrations in billfishes (μg/g) of the world

Tissue/species	Number	Cd	Pb	Cu	Zn	Area	Reference
				Muscle			
				Black marlin			
Istiompax indica	42	0.9 ± 0.009	0.6 ± 0.021	0.4 ± 0.025	8.6 ± 0.287	NE Australia	Mackay et al. (1975)
				Blue marlin			
Makaira nigricans	–	0.120	1.43	1.08	34.8	Taiwan	Han et al. (1998)
				Striped marlin			
Kajikia audax	13	0.37 ± 0.40	0.35 ± 0.08	NA	NA	SE Gulf of California	Soto-Jiménez et al. (2010)
				Swordfish			
Xiphias gladius	58	0.005 ± 0.002	0.05 ± 0.01	NA	NA	Ionian Sea	Storelli et al. (2005)
X. gladius	41	1.04 ± 1.09	0.12 ± 0.12	0.64 ± 0.32	41.7 ± 34.7	Mozambique Channel	Kojadinovic et al. (2007)
X. gladius	7	0.60 ± 0.45	0.01 ± 0.04	0.65 ± 0.46	73.5 ± 49.8	Reunion Island	Kojadinovic et al. (2007)
X. gladius	37	0.08 ± 0.01	<0.1	NA	NA	Madrid, Spain	Herreros et al. (2008)
X. gladius	12	0.158 ± 0.080	1.049 ± 0.358	NA	NA	Ionian sea	Damiano et al. (2011)
X. gladius	10	0.101 ± 0.054	1.160 ± 0.747	NA	NA	S Tyrrhenian sea	Damiano et al. (2011)
X. gladius	12	0.116 ± 0.134	1.358 ± 0.916	NA	NA	Central Tyrrhenian sea	Damiano et al. (2011)
X. gladius	11	0.045 ± 0.032	1.078 ± 0.495	NA	NA	NW Atlantic	Damiano et al. (2011)
X. gladius	11	0.042 ± 0.041	0.968 ± 0.646	NA	NA	North-central Atlantic	Damiano et al. (2011)
				Sailfish			
Istiophorus platypterus	17	0.55 ± 0.37	0.36 ± 0.29	NA	NA	SE Gulf of California	Soto-Jiménez et al. (2010)
I. platypterus	67	0.434 ± 0.099	0.025 ± 0.001	0.461 ± 0.026	15.05 ± 1.24	SE Gulf of California	This study
				Liver			
				Black marlin			
I. indica	42	9.2 ± 2.10	0.7 ± 0.031	4.6 ± 0.770	47.5 ± 9.84	NE Australia	Mackay et al. (1975)
				Swordfish			
X. gladius	192	1–28	0–1.6	NA	NA	Strait of Messina	Fossi et al. (2004)
X. gladius	58	0.16 ± 0.07	0.09 ± 0.01	NA	NA	Ionian Sea	Storelli et al. (2005)
X. gladius	42	163 ± 178	0.18 ± 0.19	54.7 ± 31.5	213 ± 73	Mozambique Channel	Kojadinovic et al. (2007)
X. gladius	14	169 ± 156	0.09 ± 0.08	65.4 ± 102.6	239 ± 45	Reunion Island	Kojadinovic et al. (2007)
				Sailfish			
I. platypterus	67	95.1 ± 11.0	0.047 ± 0.004	39.7 ± 2.6	119.1 ± 7.6	SE Gulf of California	This study
				Gonads			
				Sailfish			
I. platypterus	63	2.16 ± 0.38	0.033 ± 0.003	2.08 ± 0.14	96.8 ± 7.8	SE Gulf of California	This study

NA not analyzed

metallothionein synthesis that contributes to the bioaccumulation of Zn, Cu, and other non-essential metals (Liu et al., 2014). In addition, metals are intensively metabolized in the gonad because the most effective mechanisms of heavy metal detoxification take place there (Křížková et al., 2007).

In the muscle, bioaccumulation of the four elements was the lowest; levels of essential metals (Zn and Cu) were higher than non-essential metals (Cd and Pb). In other species of the family Istiophoridae like the black marlin (*I. indica*), the muscle presented the same sequence of essential metals (Zn > Cu) (Mackay et al., 1975) with respect to the non-essential metals; striped marlin (*Kajikia audax*) and sailfish (*I. platypterus*) also showed the same tendency of this study Cd > Pb (Table 3). The lower levels of Zn, Cu, Cd, and Pb in the muscle tissue are related to the proportion of muscle to the fish body mass; this may act as a terminal reservoir that gradually accumulates metals from other organs (Liu et al., 2014). Also, it may reflect low levels of metallothionein (Allen-Gil and Martynov 1995). Generally, fish muscle contains a balanced supply of micronutrients like Ca, P, K, Na, Mg, Fe, Mn, F, Zn, and Cu (Márquez et al., 1998).

Metal concentrations found in the edible muscle of sailfish, *I. platypterus*, were compared with national and international standards. It was found that about 28 % of the *I. platypterus* samples exhibited concentrations of Cd higher than the Mexican permissible limit (SEGOB 2011), WHO (FAO/WHO 1972), and FDA (FDA 1993a, 1993b), and more than 40 % were above the European Union limits (CREC 2006). In the case of Pb and Cu, none of the muscle samples reached the limits established (Official Mexican Standard, WHO, FDA and EU for Pb; Australia, India, and New Zealand for Cu (Nauen 1983)). Muscular levels of Zn did not exceed the Australia legal limit; however, using the guideline value adopted by India and New Zealand, about 3 % of samples exceeded such value (Fig. 2). Guidelines were established by different countries to serve as a reference of the levels of certain elements (e.g., Cd, Pb, Cu, and Zn) in fishery products for trading purposes and for protecting human health. In this context, Soto-Jimenez et al. (2010) found that sailfish from the Southeast Gulf of California exceeds partially the permissible limits (for Cd, 40 % the FDA limits, 90 % EU and WHO limits, and 20 % the Mexican limit; for Pb, 70 % the EU and WHO limits), but in higher percentages than in this study. From these results, it is clear that the consumption of the muscle of sailfish may represent some human health implications because the different established limits were exceeded, regards to Cd (28–40 % of samples) and just in a few the situation of Zn (3 %) content.

Influence of sex and body size

Gender classification in this study has shown that males and females of *I. platypterus* tend to bioaccumulate non-essential metals similarly ($p > 0.05$) in the liver, gonad, and muscle. For Cu and Zn, only the gonad showed a difference in bioaccumulation; females had the greatest levels (Table 2). Sexually mature fish needs to develop its gonad (eggs and sperm) for the reproduction process (FAO 1999). The process of formation and maturation of the egg (oogenesis) causes the gonad of females to accumulate a larger amount of Zn and Cu, due to redistribution of these metals from the liver to the ovaries, which are bound to metallothioneins and later released at the onset of oogenesis to serve as a cofactor in different enzymes (Olsson et al., 1990; Hogstrand et al., 1996). Furthermore, Zn and Cu are transferred from the liver to the ovaries through vitellogenin (Ghosh and Thomas 1995; Montorzi et al., 1995; Hogstrand et al., 1996), which is a complex glycophospholipoprotein that is specific to female egg-laying vertebrates (amphibians, birds, fish, and reptiles). During the ovarian maturation cycle, the synthesis of the complex takes place in the liver, inducing stimulation of ovarian estrogens, of which the most important is estradiol (Davail et al., 1998). Once the vitellogenin is secreted by the liver, it is transported via the bloodstream to the ovary where it is selectively taken up by the oocytes; the vitellogenin is cleaved into two phosphorous protein (lipovitellin and phosvitin), which act as carriers for lipids, phosphorus, and metals to the yolk and serve as a nutrient source during embryonic development (Redshaw and Follet 1971; Carnevali and Belvedere 1991). Mommsen and Walsh (1988) indicated that vitellogenin develops functions as a carrier protein of phosphate, lipids, carbohydrates, and metals (Ca, Fe, Cu, Mg) which are incorporated to the oocytes. Ghosh and Thomas (1995) found that Ca, Zn, Fe, Cu, and Mg are bound to vitellogenin, while Olsson et al. (1990) noted that Zn has been found in the pelletable membrane fraction of the oocyte. Therefore, female sailfish accumulate mostly Zn and Cu in the gonad for reproductive purposes and appropriate development of fish embryos.

Essential metals are generally regulated by metabolic processes in the body, so in many case they do not correlate with length or weight (Kojadinovic et al., 2007; Jakimska et al., 2011). In this study, only Zn levels in the liver and muscle were significantly ($p < 0.05$) correlated with the length and weight, respectively (Table 4). For non-essential metals in the liver and gonad, Cd levels were correlated ($p < 0.05$) with the length and weight, while Pb correlations were found between the gonad and length and weight (Table 4). The results of this study are contrasting with the results of Mackay et al. (1975) where correlations were not found between none of all these factors in the black marlin. On the other hand, Damiano et al. (2011) found a significantly positive correlation between the length and levels of Cd and Pb in the muscle of the swordfish. These discrepancies may be due to the differences in length and weight of the specimens analyzed in each study.

Metal concentrations in the stomach contents

From a total of 67 sampled organisms, 53 stomachs contained food and 14 were empty. According to the percentage of the index of relative importance (%IRI), *I. platypterus* caught in the southeastern Gulf of California feeds mainly on the fishes *Balistes polylepis* (51.96 %) and *Fistularia corneta* (15.41 %), and the cephalopods *Dosidicus gigas* (12.52 %) and *Argonauta* spp. (7.05 %) (Table 5). The ANOSIM analysis indicated that the diets of males and females were similar ($R = 0.065$; $p = 0.089$). Levels of Cd, Pb, Cu, and Zn in the preys of *I. platypterus* were highly variable (Table 5). The highest Cd and Pb levels were found in the cephalopod *Argonauta* spp. with average concentrations of 11.41 ± 0.95 μg/g for Cd and 0.057 ± 0.006 μg/g for Pb. The cephalopod *D. gigas* showed the maximum Cu levels with 4.35 ± 0.34 μg/g (ww), and the fishes of the family Clupeidae presented the highest Zn levels with 86.6 ± 0.35 μg/g. The minimum Cd, Pb, Cu, and Zn

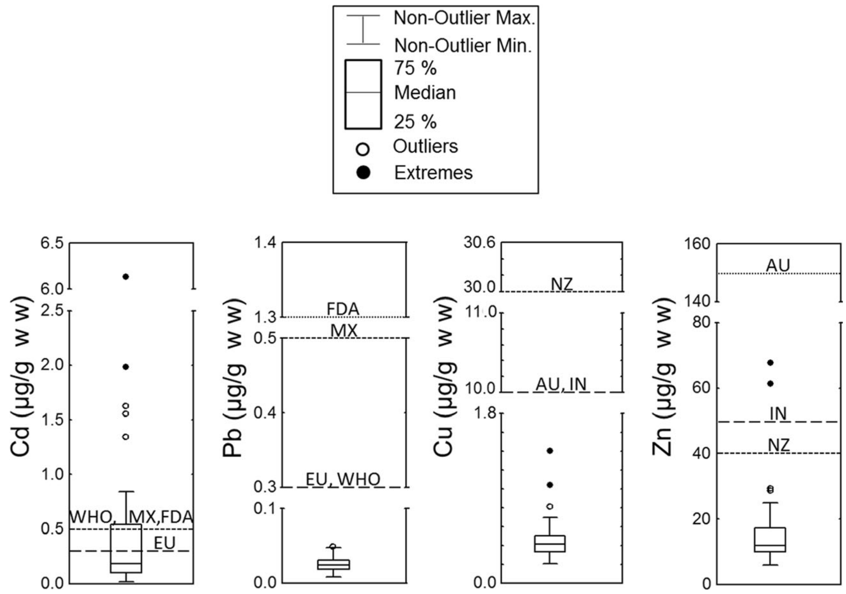

Fig. 2 Elemental levels (μg/g ww) in muscle of sailfish *I. platypterus* and the guidance values for Cd, Pb, Cu, and Zn. Guidance values correspond to the World Health Organization (*WHO*), Official Mexican Standard (*MX*), U.S. Food and Drug Administration (*FDA*), European Union (*EU*), New Zealand (*NZ*), Australia (*AU*), and India (*IN*)

concentrations were found in the fish *Coryphaena hippurus* with 0.081, 0.002, 0.204, and 3.23 μg/g, respectively.

There are several causes of the variation of Cd, Pb, Cu, and Zn concentrations in the prey organisms of *I. platypterus*. The cephalopods are able to accumulate high concentrations of metals in their tissues (Miramand and Bentley 1992; Bustamante et al., 1998) because they inhabit in the deep sea, seamounts, open water, continental slopes, minimum oxygen zones, and areas influenced by hydrothermal vents (Hoving et al., 2014). The location where the sailfish were captured is a feeding area; thus, cephalopods could be an important route of metal transference because at the mouth of the Gulf of California is located the Alarcon Ridge in which vigorous hydrothermal circulation has been reported in the east flank (Fisher et al., 2001). In hydrothermal fields, the habitat is characterized by the presence of metalliferous deposits (Fe, Ni, Cu, Zn, Cd, Pb, and Hg) and hydrothermal fluids which are enriched in metals; therefore, filtration and ingestion of metal-rich food organisms or particulate matter may serve as a pathway for metal bioaccumulation (Ruelas-Inzunza et al., 2003). Another process that occurs in the marine environment is the upwelling; this brings nutrients and trace metals (e.g., Fe, Zn, Cu, Cd) to the surface waters where phytoplankton grow, so the elemental composition of the phytoplankton can be transferred up the food chain through primary and secondary producers, to provide the bulk of the food base for scombrids, carangids, and clupeids (Elderfield et al., 2006; Prince and Goodyear 2006). On the other hand, a factor against metal accumulation is the rapid growth rate and short life span of organisms, as is the case of the fish *C. hippurus* (Adams 2009). Hence, many environmental factors and biological factors such as sex, age, health status, body conditions, life cycle, and feeding habits would also influence metal deposition in animal tissues (Cheng et al., 2013; Authman et al., 2015).

Table 4 Spearman correlations (*R*) between Cd, Pb, Cu, and Zn in muscle, liver, and gonads of *I. platypterus*

	LJFL		Weight	
	Spearman R	*p* value	Spearman R	*p* value
Cd_{Muscle}	0.15	0.240	0.08	0.503
Cd_{Liver}	*0.37*	*0.002*	*0.35*	*0.004*
Cd_{Gonad}	0.24	0.055	*0.28*	*0.029*
Pb_{Muscle}	0.04	0.776	0.05	0.700
Pb_{Liver}	−0.04	0.755	−0.09	0.493
Pb_{Gonad}	*0.36*	*0.004*	*0.31*	*0.014*
Cu_{Muscle}	0.02	0.879	0.02	0.863
Cu_{Liver}	0.21	0.095	0.16	0.203
Cu_{Gonad}	0.08	0.544	0.09	0.507
Zn_{Muscle}	0.20	0.111	*0.27*	*0.030*
Zn_{Liver}	*0.27*	*0.030*	0.24	0.052
Zn_{Gonad}	0.03	0.797	0.07	0.598

Entries in italics indicate significance level ($p < 0.05$)

LJFL lower jaw fork length

Biomagnification factors (BMFs) of trace elements

From the estimated biomagnification factors of the examined elements, only Pb was biomagnified in *I. platypterus* obtaining a BMF = 1.85 (Table 6). Thus, the present study provides evidence of Pb biomagnification as has been reported previously in the Gulf of California region in other trophic nets (Ruelas-Inzunza and Páez-Osuna 2008; Ruelas-Inzunza et al., 2014). The behavior of Cu, Zn, and Cd was similar to results in a subtropical coastal lagoon in the southeastern Gulf of California (Estero de Urías), which had ranges of metal

Table 5 Composition of stomach content and levels of Cd, Pb, Cu, and Zn (mean ± SE µg/g; ww basis) in *I. platypterus* from the SE Gulf of California during 2011–2013

Species or group	%*F*	%*N*	%*W*	IRI	%IRI	Number	Cd	Pb	Cu	Zn
Cephalopods										
Ommastrephidae										
Dosidicus gigas	*41.51*	*4.93*	*17.26*	*921.2*	*12.52*	88	7.430 ± 0.751	0.015 ± 0.001	4.35 ± 0.34	23.9 ± 1.24
Argonautidae										
Argonauta spp.	*47.17*	*8.29*	*2.70*	*518.6*	*7.05*	148	11.412 ± 0.950	0.057 ± 0.006	3.13 ± 0.24	45.9 ± 2.12
Teleost fishes										
Clupeidae	1.89	1.46	0.05	2.8	0.04	26	0.878 ± 0.001	0.026 ± 0.000	1.44 ± 0.01	86.6 ± 0.35
Belonidae										
Tylosurus crocodilus fodiator	9.43	1.12	0.09	11.4	0.15	20	0.947 ± 0.060	0.043 ± 0.003	1.74 ± 0.08	56.4 ± 0.96
Hemiramphidae										
Hemiramphus saltator	9.43	0.25	0.84	20.0	0.27	5	5.091 ± 0.583	0.027 ± 0.002	2.71 ± 0.23	39.1 ± 1.42
Exocoetidae	5.66	1.18	0.20	7.8	0.11	21	2.192 ± 0.080	0.023 ± 0.001	1.57 ± 0.03	85.5 ± 2.92
Fistulariidae										
Fistularia corneta	*26.42*	*30.70*	*12.22*	*1133.8*	*15.41*	548	2.072 ± 0.182	0.018 ± 0.000	0.60 ± 0.03	54.9 ± 1.42
Priacanthidae										
Pristigenys serrula	1.89	0.11	0.20	0.6	0.01	2	5.013 ± 0.141	0.008 ± 0.000	0.62 ± 0.02	10.2 ± 0.29
Carangidae										
Caranx spp.	*22.64*	*10.92*	*4.61*	*351.6*	*4.78*	195	2.320 ± 0.190	0.024 ± 0.002	1.80 ± 0.06	41.2 ± 2.06
Caranx caballus	13.21	1.29	3.22	59.5	0.81	23	0.516 ± 0.020	0.016 ± 0.001	0.93 ± 0.02	18.8 ± 0.23
Caranx vinctus	1.89	0.56	0.26	1.5	0.02	10	0.437 ± 0.001	0.024 ± 0.000	1.59 ± 0.04	39.3 ± 0.28
Decapterus spp.	1.89	0.56	0.91	2.8	0.04	10	1.030 ± 0.011	0.013 ± 0.000	1.59 ± 0.01	15.9 ± 0.19
Selene brevoortii	1.89	0.73	0.26	1.9	0.03	13	0.800 ± 0.010	0.027 ± 0.000	0.87 ± 0.01	39.5 ± 0.37
Coryphaenidae										
Coryphaena hippurus	1.89	0.06	19.73	37.3	0.51	1	0.081	0.002	0.20	3.2
Mugilidae										
Mugil cephalus	3.77	0.11	*1.26*	5.2	0.07	2	0.204 ± 0.000	0.032 ± 0.001	1.38 ± 0.08	17.7 ± 0.14
Scombridae	*24.53*	*4.87*	*8.59*	*330.1*	*4.49*	87	3.981 ± 0.582	0.015 ± 0.002	1.29 ± 0.12	22.9 ± 1.49
Auxis spp.	3.77	0.90	2.06	11.2	0.15	16	2.842 ± 0.200	0.014 ± 0.000	2.69 ± 0.02	26.7 ± 0.05
Scomber japonicus	*16.98*	*1.74*	*4.86*	*112.0*	*1.52*	31	4.504 ± 0.551	0.012 ± 0.001	2.94 ± 0.14	29.3 ± 1.29
Balistidae										
Balistes polylepis	*79.25*	*29.36*	*18.89*	*3823.1*	*51.96*	524	5.282 ± 1.020	0.023 ± 0.001	1.29 ± 0.10	64.2 ± 2.72
Monacanthidae	1.89	0.17	0.01	0.3	0.00	3	8.333 ± 0.011	0.037 ± 0.000	1.42 ± 0.01	74.4 ± 0.02
Tetraodontidae										
Lagocephalus lagocephalus	3.77	0.11	0.07	0.7	0.01	2	0.907 ± 0.008	0.025 ± 0.000	0.99 ± 0.01	51.1 ± 0.19
Sphoeroides spp.	1.89	0.22	0.09	0.6	0.01	4	0.661 ± 0.006	0.017 ± 0.000	0.85 ± 0.01	68.9 ± 0.64
Fish remains	3.77	0.34	0.63	3.6	0.05	6	1.080 ± 0.012	0.020 ± 0.001	0.90 ± 0.03	34.1 ± 2.29
				Total	100					

Values in italics represent the most important prey items in *I. platypterus* diet based on the index of relative importance (IRI; %*N* number expressed as a percentage of all prey items; %*W* wet weight expressed as percentage of the total weight o all prey items; %*F* percentage frequency of occurrence)

n number of samples, *SE* standard error

concentrations higher than the levels of the open sea and other coastal waters (Jara-Marini et al., 2009). In this lagoon, in fact there was no evidence of biomagnification with these three metals. Nevertheless, Amiard et al. (1980), Metayer et al. (1980), and Ruelas-Inzunza and Páez-Osuna (2008) have reported biomagnification of these metals in some trophic links. Therefore, the results of this research demonstrate the contrasting behavior of Cd, Pb, Cu, and Zn biomagnification through the marine trophic levels, such as have been previously argued (Wang 2002) and can be noticed in Table 6. It is evident that biomagnification will depend on components of the diet of the species (feeding habits), influx rates from food, rate constants of loss, physiological characteristics (existence of proteins like metallothioneins), biological role, and

Table 6 Cd, Pb, Cu, and Zn biomagnification factors of some studies in marine/estuarine food webs

Aquatic predators	TL	Tissue	Cd	Pb	Cu	Zn	Location	Reference
Syngnathus rostellatus	NA	Whole	0.07	0.28	0.23	1.43	Loire estuary, Fr	Amiard et al. (1980)
Engraulis encrasicolus	NA	Whole	0.48	0.13	0.44	1.29	Loire estuary, Fr	Amiard et al. (1980)
Sprattus sprattus	NA	Whole	0.17–0.88	0.04–0.28	0.20–0.48	1.09–1.90	Loire estuary, Fr	Amiard et al. (1980)
Merlangius merlangus	NA	Whole	0.37	0.30	0.16	0.74	Loire estuary, Fr	Metayer et al. (1980)
Gadus luscus	NA	Whole	0.08	0.42	0.48	0.81	Loire estuary, Fr	Metayer et al. (1980)
Stizostedion lucioperca	NA	Whole	1.63	0.37	1.32	1.05	Loire estuary, Fr	Metayer et al. (1980)
Lutjanus colorado	NA	Muscle	0.7, 0.4, 0.006	1.3, 1.4, 2.6	–	1.1, 0.3, 0.4	Altata-Ensenada del Pabellón, Mx	Ruelas-Inzunza and Páez-Osuna (2008)
Cynoscion xanthulus	NA	Muscle	1.8, 1.8, 0.3	1.1, 2.8, 5.2	–	1.1, 0.3, 0.4	Altata-Ensenada del Pabellón, Mx	Ruelas-Inzunza and Páez-Osuna (2008)
Lutjanus argentiventris	4.2	Whole	<1	<1	0.09, 0.20	0.25, 0.12	SE Gulf of California, Mx	Jara-Marini et al. (2009)
Gerres cinereus	4.1	Whole	<1	<1	0.03, 0.12	0.67, 0.25	SE Gulf of California, Mx	Jara-Marini et al. (2009)
Clupea harengus	3.98	Whole	0.79	0.89	0.98	0.91	Baltic Sea[b]	Nfon et al. (2009)
Katsuwonus pelamis	3.94	Muscle	0.01	NA	NA	NA	E Pacific Ocean	Ruelas-Inzunza et al. (2014)
Thunnus albacares	4.60	Muscle	0.01	1.46	NA	NA	E Pacific Ocean	Ruelas-Inzunza et al. (2014)
I. platypterus	5.1[a]	Muscle	0.61	1.85	0.44	0.66	SE Gulf of California, Mx	This study

TL trophic level, *NA* not available, *Fr* France, *Mx* Mexico

[a] Trophic level from Olson and Waters (2003)

[b] Sweden, Finland, Estonia, Latvia, Norway, Poland, Germany, and Denmark

physico-chemical state (speciation) of available metals in marine organisms (Amiard-Triquet et al., 1993; Luoma and Rainbow 2005).

Conclusions

The results of this study show that *I. platypterus* can accumulate metals in their tissues; levels of Cd and Zn in some specimens were above the guideline values. The sequence of elemental concentrations in the liver and gonad was Zn > Cd > Cu > Pb, in the muscle it was Zn > Cu > Cd > Pb. Males and females of this species tend to accumulate similar levels of Cd and Pb in the liver, gonad, and muscle. For Cu and Zn, the gonad of females had the highest levels, which could be due that the mature fish needs to build up the gonad for the reproduction, and in the case of females these accumulate a larger concentration of Zn and Cu.

According to the index of relative importance, *I. platypterus* caught in the southeastern Gulf of California feeds mainly on the fishes *B. polylepis* and *F. corneta* and the cephalopods *D. gigas* and *Argonauta* spp. The levels of Cd, Pb, Cu, and Zn in the preys of *I. platypterus* were highly variable; the highest levels of Cd and Pb were measured in *Argonauta* spp.; Cu concentrations were highest in *D. gigas* while Zn was the most concentrated in the fishes of the family Clupeidae. The minimum Cd, Pb, Cu, and Zn concentrations were found in the fish *C. hippurus*.

The present study provides evidence of Pb biomagnification in *I. platypterus* and confirms the behavior of Cu, Zn, and Cd with respect to their biodiminution. Lead increases through the prey organisms of *I. platypterus* could jeopardize the health of marine life. However, for humans, this metal is still below the guideline values. In the case of Cd, it was found that 28–40 % of the *I. platypterus* muscle samples were higher than the national and international norms. Muscular levels of Zn exceeded about 0–3 % of the international norms. From this work and considering the presence of detectable levels of non-essential metals as Pb and Cd, it is recommended to develop monitoring studies in large predatory fish as *I. platypterus* and other ecologically relevant species in the Gulf of California, which is one of the ecosystems with the highest priority for conservation on the planet because of its rich biodiversity, high rates of biological productivity, and endemism. However, as with other ecosystems in the world, it faces numerous threats resulting primarily from overfishing and degradation of coastal habitats.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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