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Biomagnification of mercury and its antagonistic interaction with selenium in yellowfin tuna *Thunnus albacares* in the trophic web of Baja California Sur, Mexico

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ABSTRACT

Mercury and selenium concentrations were determined in muscle of 37 yellowfin tuna (*Thunnus albacares*) captured aboard of Mexican purse-seiners boats off western coast of Baja California Sur, between Punta Eugenia and Cabo Falso, from October to December 2006. Also, its prey (mainly, jumbo squid *Dosidicus gigas* and pelagic red crab *Pleuroncodes planipes*) were analyzed from the stomach contents. All the mercury values obtained were lower that mercury content recommended by standard legal limits for seafood adopted by Mexican norms (typically 0.5–1.0 $\mu g\, g^{-1}$). Mercury concentrations vary between 0.06 and 0.51 $\mu g\, g^{-1}$ in yellowfin tuna, and from 0.01 to 0.20 $\mu g\, g^{-1}$ in its prey, suggesting that mercury can accumulate in prey tissues and that of their predator. Biomagnification factors (BMF) between predator-prey associations were calculated. The BMFs were >1, indicating that mercury biomagnifies along the food web of yellowfin tuna. In all species studied there was a molar excess of selenium over mercury. The rank order of mean selenium/mercury molar ratios was for pufferfish (42.62) > diamond squid (15.09) > yellowfin tuna (10.29) > pelagic red crab (10.05) > panama lightfish (9.54) > jumbo squid (8.91). The selenium health benefit value (Se-HBV) was calculated to have an improved understanding of the health benefits and risk of fish consumption.

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1. Introduction

Mercury (Hg) contamination is a problem worldwide, since it is a persistent contaminant and is widely distributed in the environment, having natural as well as anthropogenic sources. The most common mercury forms in the environment are elemental mercury (Hg^0), mercuric mercury (Hg^{2+}) and methylmercury ($HgCH_3^+$). The environmental risk of mercury is high, because geogenic mercury can be easily transformed into other chemical forms, which can be volatile and be transported great distances in the atmosphere (Yang et al., 2008). Once in terrestrial or aquatic systems, Hg can accumulate in the trophic web (Páez-Osuna et al., 2011). High mercury concentrations have been recorded in the edible parts of pelagic fish of recreational, economical and cultural importance to millions of people worldwide (García-Hernández et al., 2007; Soto-Jiménez et al., 2010; Escobar-Sánchez et al., 2011; Ordiano-Flores et al., 2011). High concentrations are related to the higher trophic level these fish occupy, the type of food they eat, and the effect of biomagnifications of Hg through the trophic chain.

Methylmercury (MeHg), one of the organic forms of Hg that bioaccumulates and comprises 95–97 percent of the Hg in fish muscle tissue (Bloom, 1992), is one of the most readily absorbed and bioavailable Hg forms found in the nature. Because total Hg concentration usually approximates that of MeHg in fish muscle tissue (Bloom, 1992) and total Hg is much easier to measure. Total Hg analyses are recommended for fish tissue surveys (U.S. Enviromental Protection Agency, 1997). Because, humans can be exposed to Hg mainly by consumption of fish from mercury-polluted waters, in 2001, the U.S. Environmental Protection Agency (EPA) established a fish tissue-based water quality criterion of 0.3 μg MeHg g^{-1} wet weight for eatable fish tissue (usually filet) as a protection to human consumers against MeHg toxicity (U.S. Environmental Protection Agency 2001). The agencies of health in México have established maximum limits for mercury in fish from 0.5 for seafood to 1.0 $\mu g\, g^{-1}$ for large fish (Secretaría de Salud, 2009).

Selenium (Se) is an element that is normally found in high levels in seafood, and may protect against Hg toxicity without

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specifically modulating MeHg absorption or excretion (Yang et al., 2008; Khan and Wang, 2009). Like mercury (mainly MeHg), selenium is acquired by organisms when they consume food and water, and is absorbed as selenite, selenate or organic Se (Yang et al., 2008). Although the interaction between Hg and Se showed an antagonistic effect, additive or even synergistic effects of Hg and Se have also been reported in the literature (Dang and Wang, 2011). For Se, an essential element for animals and humans, will cause toxic effects when the concentration is elevated above what is considered optimal. Assuming the formation of a 1:1 M ratio Hg/Se compound that is biologically inert, an antagonism or synergistic effect depends on the sensitivity of the organ/organism (which determines the threshold concentrations $[Hg]_{toxicity}$, $[Se]_{deficiency}$, and $[Se]_{toxicity}$), and the relative concentrations of Hg and Se (Khan and Wang, 2009). However, differences across studies in the forms of Se and Hg, and the route and duration of exposure make a difficult interpretation. While several animal studies have shown protection against inorganic Hg toxicity by selenite, there is no evidence showing protection against MeHg toxicity by the organic Se compounds, such as selenomethione or selenocysteine, that are the forms of Se commonly found in the human diet. There is no human data that support a protective role for Se with respect to Hg toxicity (Mergler et al., 2007).

As Se may mitigate the toxicity of Hg, the molar ratio of Hg/Se has been suggested to be one essential criterion for assessing the true health risks posed by Se (Kaneko and Ralston 2007; Ralston et al., 2007). Kaneko and Ralston (2007) proposed a selenium health benefit value (Se-HBV) index to help identify fish species with low Hg levels and high Se content. Recent studies show a high molar ratio Se/Hg in the edible parts of different fish species highly consumed by humans, such as yellowfin tuna, with a higher Se-HBV index (Fang et al., 2011). However, not everyone agrees with the Se-HBV, because the lack of enough research on different species and ratio between them. Therefore, selenium presence in commercial marine fish and its significant protection effect against Hg are two important aspects that should be considered in regards to safety of marine product consumption.

In this study, mercury concentrations were determined in yellowfin tuna *Thunnus albacares* (a top predator important for Mexican fisheries), and its main prey (lower trophic level species), in order to determine the content and trophic increment of mercury in the tuna trophic chain. Furthermore, because aquatic organisms bioaccumulate MeHg, and Se moderates MeHg toxicity effects, we determined Se for examines the antagonist interaction with Hg, and the selenium health benefit value (Se-HBV) was calculated in order to have an improved understanding of the health benefits and risk of fish consumption.

2. Material and methods

2.1. Sample collection

In this study, a total of 37 specimens of yellowfin tuna were sampled off the western coast of the Baja California Sur peninsula, between Punta Eugenia and Cabo Falso (Fig. 1). The geographic coordinates and the number of animals sampling are presented in Table 1. Sampling was carried out by technical observers of the Inter-American Tropical Tuna Commission (IATTC) aboard in Mexican purse-seiners boats from October to December 2006. During sampling, every specimen was measured. The fork length (FL; from the tip of the top jaw to the fork of caudal fin) varied from 605 to 942 mm. Muscle tissue was taken from each fish by dissecting a portion (~15 g) of red muscle from the frontal area of the dorsal muscle mass (mainly located under the skin between the first dorsal fin and the lateral line). Stomach contents were extracted from each specimen by dissecting and kept in previously tagged plastic bags for posterior identification of the main prey in the diet of yellowfin tuna (Galván, 1988; Alatorre, 2007). Muscle tissue samples and stomach contents were deep-frozen after capture.

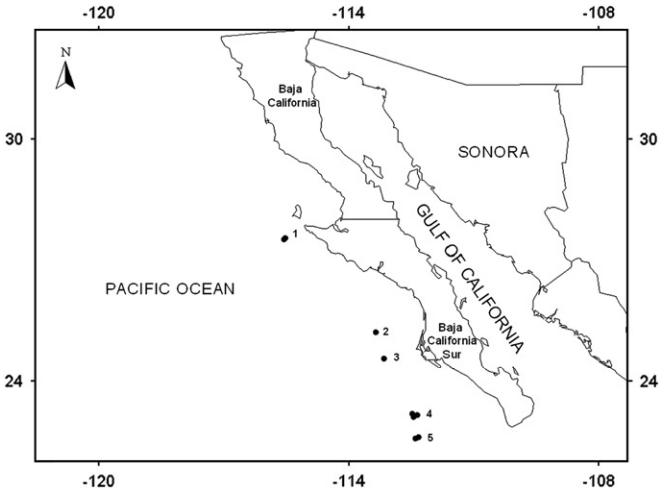

Fig. 1. Map of Baja California Sur, Mexico showing the sampling sites (black dots) of yellowfin tuna: 1 Punta Eugenia; 2 Boca de Soledad; 3 Bahía Magdalena; 4 Todos Santos; 6 Cabo Falso. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Name, geographic position, and simple size for each of the locations sampled in this study.

Sites	Location	Sample size
Punta Eugenia	27°52′N, 115°51′W	5
Boca de Soledad	25°21′N, 113°28′W	6
Bahía Magdalena	24°56′N, 113°07′W	6
Todos Santos	23°14′N, 112°25′W	3
Cabo Falso	22°57′N, 112°30′W	17

2.2. Sample processing and metal analysis

The identification of prey was made using specialized taxonomic keys (Fish Ecology Laboratory in CICIMAR-IPN). Prey that was in a minimal digestion state was selected (fresh samples). There was a very small sample size for most prey species analyzed, with the exception of jumbo squid *Dosidicus gigas* and pelagic red crab *Pleuroncodes planipes*. Specifically, fifteen jumbo squid, five pelagic red crab, two Panama lightfish *Vinciguerria lucetia*, two pufferfish *Lagocephalus lagocephalus*, three diamond squid *Thysanoteuthis rhombus*, and two purple squid *Sthenotheuthis oualaniensis* were collected. Muscle tissue from prey fish species was sampled from the same area than yellowfin tuna. Cephalopod muscle tissue was collected from each specimen by dissecting a portion (~15 g) of muscle from the frontal area of the dorsal mantle mass. Small organisms such as crustaceans were grouped to obtain a large enough sample.

Samples free from residue were dehydrated in an oven at 60 °C during 36 h. They were later ground using an agate mortar. Dry homogenized samples were stored in previously tagged polyethylene bags and stored in a dehydrator. A closed acid digestion process was carried out using a microwave oven (CEM-MDS, 2000). Subsamples of dry muscular tissue (~ 0.5 g) were placed in digestion vessels, and 3 mL of concentrated nitric acid, 1 mL hydrogen peroxide and 2 mL deionized double distilled water (Milli-Q water purification system) were added. The digestion process included 5 microwave stages, each one lasting 15 min and using 80 percent power and pressures of 10, 20, 40, 84 and 100 psi (pounds per square inch), respectively. Once the samples were cool, the digestion solutions were transferred to polyethylene vials; they were diluted in a known volume of deionized water and stored refrigerated for posterior metal analysis.

Atomic absorption spectrophotometer analysis (AAS) for total mercury (T–Hg) and selenium readings was carried out in Veterinary faculty in Universidad Nacional Autonoma de Mexico, using a Perkin–Elmer Analyst 100 apparatus, coupled to a hydride generator (Perkin–Elmer MHS-10). Absorbances were calibrated using the linear regression line for three solutions of known concentration for each metal. Hg was measured using the AAS equipment, using flameless, cold–vapor techniques to elementary mercury. Se was measured by generation of hot volatile Se–hydride vapors. Equipment operating conditions for the determination of each metal were set according to the operation manual. Using regression analysis, the absorbance readings were compared with the metal concentrations. Mercury and selenium concentrations were expressed in micrograms per gram dry weight ($\mu g\, g^{-1}$ dw) and transformed to wet weight ($\mu g\, \mu g\, g^{-1}$ ww), taking into account water loss during the dehydration process. Controls and standard reference material (IAEA-407

of fish homogenate, from the International Atomic Agency Monaco) were included in each digestion batch to verify the accuracy and precision of the extraction method. Values obtained from reference material ($0.20 \pm 0.05\ \mu g\ g^{-1}$ for Hg and $2.00 \pm 0.50\ \mu g\ g^{-1}$ for Se in dry weight; $n=6$) were satisfactory with certified values (rate: 0.22–0.23 $\mu g\ g^{-1}$ for mercury and 2.70–2.96 $\mu g\ g^{-1}$ for selenium). For analyses of standard concentrations of Hg and Se, the coefficient of variation (percent CV) was 3.63 for five replicates measures.

2.3. Data processing

Due to limited sample size for each species, statistical analyses were only performed on yellowfin tuna, jumbo squid and pelagic red crab ($n \geq 5$). To assess relationships between predator–prey, species were pooled together for biomagnification analyses. Analysis nonparametric (Mann–Whitney U test) were undertaken to establish respective significant differences within the dataset. We used a regression analysis on mercury concentrations versus selenium concentrations across the different species to demonstrate the relationship of increased levels of mercury versus the levels selenium. All the statistical analyses were carried out with SPSS 17 and SigmaPlot 10 software.

To examine the extent in which mercury biomagnifies throughout the food web, we calculated biomagnifications factors (BMF) between various prey and yellowfin tuna. This biomagnification factor can involve organisms of a known trophic level. Such factors have been applied to a number of higher-order predators (Gray, 2002) using the following equation:

$$BMF = [THg]_{predator} / [THg]_{prey}$$

To gain a better description and integration of the specific nutritional benefits of selenium regarding the potential risk of exposure to mercury from food consumption, the selenium health benefit value (Se-HBV) proposed by Kaneko and Ralston (2007) was calculated:

$$\text{Se-HBV} = (\text{Se/Hg molar ratio} \times \text{total Se}) - (\text{Hg/Se molar ratio} \times \text{total Hg})$$

The mass concentrations ($\mu g\ g^{-1}$) of each individual were transformed to molar concentration (micromoles per kilogram), and the molar ratios of Hg/Se and Se/Hg were calculated for each sample. Selenium molar excess (free selenium) in relation to mercury in the samples was calculated by subtracting the molar concentration of mercury divided by the selenium molar concentration. The average values were used to establish the selenium health benefit value for yellowfin tuna and each of its prey.

3. Results

3.1. Mercury content and biomagnification

The concentrations of Hg in the muscle tissue of yellowfin tuna and species of prey are showed in Fig. 2. Total Hg levels ranged from 0.01 to 0.51 $\mu g\ g^{-1}$ for yellowfin tuna and from 0.01 to 0.20 $\mu g\ g^{-1}$ for all species of prey. Yellowfin tuna recorded the highest concentrations of mercury (average $\pm$ sd: $0.15 \pm 0.10\ \mu g\ g^{-1}$). Among species prey, purple squid *S. oualaniensis* recorded the highest concentration of mercury ($0.10 \pm 0.08\ \mu g\ g^{-1}$), followed by the jumbo squid *Dosidicus gigas* ($0.06 \pm 0.05\ \mu g\ g^{-1}$), and Panama lighfish *V. lucetia* ($0.05 \pm 0.03\ \mu g\ g^{-1}$). The lowest levels of mercury were recorded in diamond squid *T. rhombus* ($0.03 \pm 0.02\ \mu g\ g^{-1}$), pufferfish *L. lagocephalus* ($0.03 \pm 0.02\ \mu g\ g^{-1}$) and pelagic red crab *P. planipes* ($0.03 \pm 0.02\ \mu g\ g^{-1}$). When yellowfin tuna, jumbo squid and pelagic red crab were analysed together, interspecific differences were evident between yellowfin tuna and its prey (Mann–Whitney U, $p < 0.05$). However, Hg concentrations were not significantly different between jumbo squid and pelagic red crab (Mann–Whitney U Test, $p=0.41$).

Biomagnification factors (BMF) calculated for yellowfin tuna and all prey pooled together were highly variable from predator-prey combination (Fig. 3). All BMFs were >1, indicating absolute biomagnifications. Higher BMFs were generally observed between crustaceans and mesopelagic fish (species of low trophic positions) and yellowfin tuna than those between cephalopods (secondary consumers) and tunas (Fig. 3). When yellowfin tuna and its prey were pooled together, mercury levels were correlated strongly with trophic position ($R_S=0.73$, $p < 0.05$). Results suggest that mercury can accumulate in prey tissues and that of their predator.

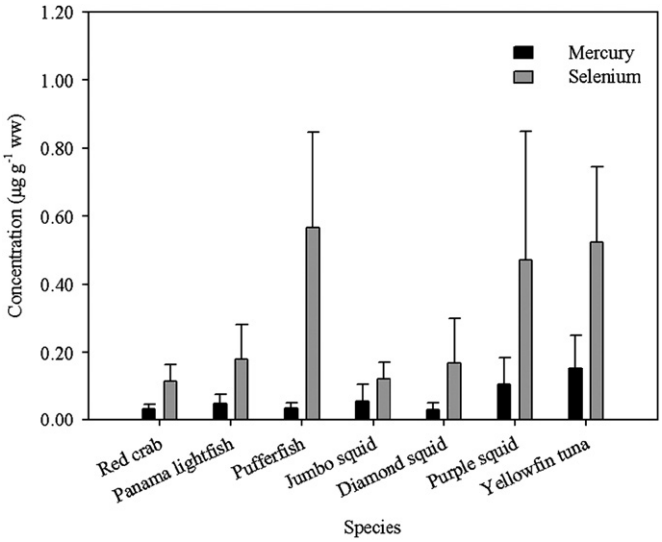

Fig. 2. Mass concentrations of mercury and selenium ($\mu g\ g^{-1}$ ww) in yellowfin tuna and their main prey from Baja California Sur, Mexico. Data are expressed as mean $\pm$ standard deviation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Selenium analysis

Higher quantities of selenium than mercury were recorded in yellowfin tuna as well as in prey (Fig. 2). The levels of selenium vary between 0.20 and 1.01 $\mu g\ g^{-1}$ in yellowfin tuna; and from 0.03 to 0.76 $\mu g\ g^{-1}$ in the species prey. The highest selenium content was recorded for the fish group, including yellowfin tuna (average $\pm$ sd: $0.52 \pm 0.22\ \mu g\ g^{-1}$), pufferfish ($0.57 \pm 0.28\ \mu g\ g^{-1}$), and Panama lightfish ($0.18 \pm 0.10\ \mu g\ g^{-1}$). The group of cephalopods had lower concentrations of selenium ($0.12 \pm 0.05\ \mu g\ g^{-1}$ for jumbo squid and $0.17 \pm 0.13\ \mu g\ g^{-1}$ for diamond squid), with the exception of purple squid ($0.47 \pm 0.38\ \mu g\ g^{-1}$). The lowest concentrations of selenium were for pelagic red crab ($0.11 \pm 0.05\ \mu g\ g^{-1}$). Selenium levels of yellowfin tuna were significantly different from pelagic red crab and jumbo squid (Mann–Whitney U Test, $p < 0.05$). However, selenium concentrations were not significantly different among prey species (Mann–Whitney U, $p > 0.05$).

Higher levels of Hg follow those of Se and the highest coincide for the same species analyzed: *P. planipes*, *T. rhombus*, *D. gigas*, *V. lucetia*, *S. oualaniensis*, and *T. albacares*. The positive correlation is significant ($R_s=0.78$, $p=0.03$; Fig. 4). Table 2 showed the molar ratios between mercury and selenium, and the molar rations between selenium and mercury; an average molar excess of selenium over mercury was recorded in yellowfin tuna and its prey. The molar rations between mercury and selenium (Hg/Se) ranged from 0.05 to 0.30 in yellowfin tuna, and from 0.02 to 0.75 in prey. The molar ratios between selenium and mercury (Se/Hg) ranged from 3.31 to 20.20 in yellowfin tuna, and from 1.34 to 42.62 in prey. Furthermore, the calculated selenium health benefit values Se-HBV is shown in Table 2. Values Se-HBV ranged from 7.87 to 244.54 for yellowfin tuna, and -0.28 to 403.16 for species prey.

4. Discussion

The mercury levels found in this study for yellowfin tuna *T. albacares* were lower and/or similar to those found in other species from other oceans (Storelli et al., 2002; Rassmussen et al., 2005; Kojadinovic et al., 2006; Kaneko and Ralston, 2007), possibly due to differences in feeding habits, growth rate and

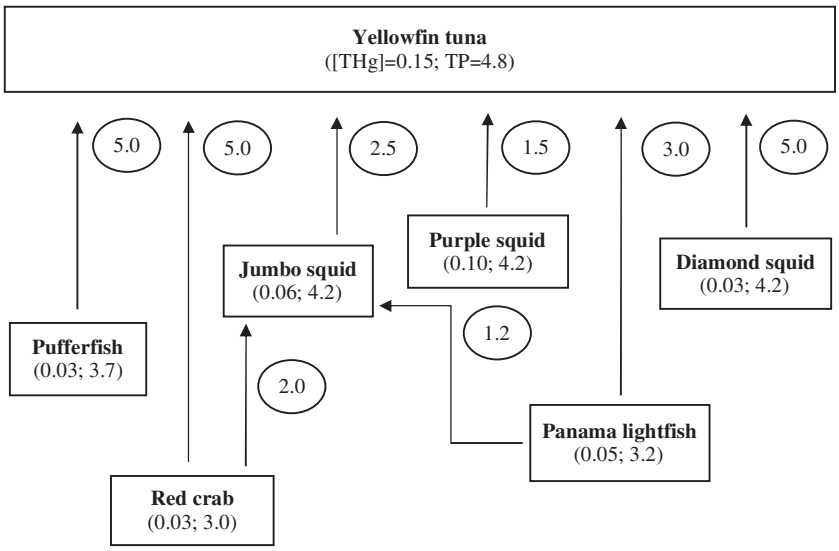

Fig. 3. Graphic representation of mercury biomagnification in the trophic chain of yellowfin tuna off the western coast of Baja California Sur, Mexico. Circles indicate biomagnification factors. The trophic position (TP) is based according to Olson and Watters (2003).

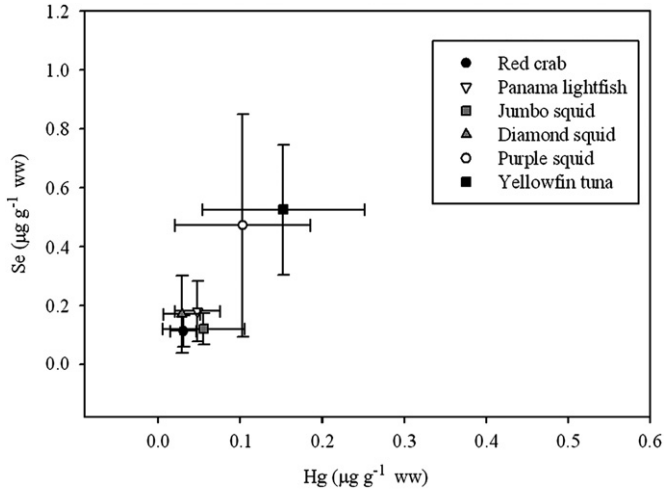

Fig. 4. Relationship between mercury and selenium concentrations for species studied.

Table 2
Molar concentrations, molar ratios of mercury and selenium, and selenium health benefit value. Values represent mean ± standard deviation.

Species	Hg (μmol kg^{-1})	Se (μmol kg^{-1})	Hg/Se molar ratio	Se/Hg molar ratio	Se-HBV
Yellowfin tuna	0.76 ± 0.49	6.64 ± 2.80	0.12	10.29	64.54
Panama lightfish	0.24 ± 0.14	2.28 ± 1.31	0.10	9.54	19.41
Pufferfish	0.17 ± 0.08	7.17 ± 3.56	0.02	42.62	298.40
Jumbo squid	0.27 ± 0.25	1.51 ± 0.67	0.21	8.91	12.82
Diamond squid	0.14 ± 0.11	2.15 ± 1.66	0.07	15.09	30.30
Purple squid	0.51 ± 0.41	5.97 ± 4.79	0.09	11.64	63.52
Red crab	0.15 ± 0.08	1.42 ± 0.67	0.11	10.05	13.26

trophic position, but higher than those reported by García-Hernández et al. (2007) for the Gulf of California for this same species (0.03 μg g^{-1}). Although analytical methods and controls were appropriate for quality control and analytical assurance purposes, this value seems lower for a mercury concentration in any tuna species. The reasons for these differences in mercury values are unknown, but are representative of mercury accumulation patterns at both sites. Off the western coast of Baja California Sur, blue shark *Prionace glauca* specimens have shown mercury concentrations over the recommended limits of Mexican norms. The Mexican norm is standard legal limit of mercury content of 1.0 μg g^{-1} for large fish and 0.5 μg g^{-1} for seafood (Secretaría de Salud, 2009). The high values of mercury in fish are possibly due to industrial discharge of metals, including mercury (Escobar-Sánchez et al., 2011). However, despite the existence of an industrial influence in the Baja California peninsula, Baja California Sur is considered a pristine area within an area containing mineral deposits that could contribute to the heavy metal concentrations in coastal waters of the Baja California peninsula (Shumilin et al., 2000, 2001). It has therefore been suggested that the main source of contaminants, included mercury, is natural in oceanic waters.

The diet of *T. albacares* analyzed in Baja California Sur is dominated by lower trophic level species such as crustaceans (pelagic red crab, pelagic crabs, etc.), molluscs (*Argonauta* sp., squid, etc.) and small fish (*Auxis* sp., Photichthyidae) (Galván, 1988; Alatorre, 2007). The prey analyzed in the present study had mercury levels lower than those of yellowfin tuna (Fig. 2), suggesting that mercury can accumulate in prey tissues and that of their predator. Furthermore, we should not overlook that the tuna is a marine organism highly migratory that move long distances and the mercury measured in muscle yellowfin tuna may have been obtained from other geographical regions with different prey. Perhaps an analysis of blood (which reflects near-term mercury exposure) rather than muscle (which sequesters mercury for years) would allow for a greater understanding of local sources. On the other hand, the analysis of biomagnification factor (BMF), which should be >1 when there is an increase in contaminant concentration between immediate trophic levels (Gray, 2002), was found in the tuna trophic chain (Fig. 3). Furthermore, Panama lightfish *V. lucetia* and red crab *P. planipes* are prey of jumbo squid *D. gigas*, among which was calculated biomagnifications factor. BMFs were equal or greater than unity, indicating biomagnifications on their prey (Fig. 3). The process of biomagnifications of mercury can, therefore, be amplified by prey items and trophic position of this species.

Reports of feeding habits of yellowfin tuna carried out by Galván (1988) and Alatorre (2007) show the jumbo squid *D. gigas* as one of the prey most consumed by yellowfin tuna off the western coast of Baja California Sur. In terms of biomass the jumbo squid should be an important source of mercury input compared to other cephalopods (i.e., purple squid *S. oualaniensis* and diamond squid *T. rhombus*). Although mercury concentrations were higher in purple squid *S. oualaniensis*, this species was not representative of the yellowfin tuna diet. This difference in mercury concentrations is expected for sources of mercury in the diet. Markaida and Sosa-Nishizaki (2003) found that Panama lighfish *V. lucetia* and pelagic red crab *P. planipes* represent only 0.8 and 5.1percent of occurrence in the stomach content of jumbo squid from the Gulf of California. Analysing sources of mercury in the diet of the jumbo squid *D. gigas*, it is worth noting that yellowfin tuna have considerable overlap in prey (Fig. 3). The initial impression is that the low levels of mercury in mantle tissue of jumbo squid *D. gigas* might be attributed to the short life span of the cephalopods (Jackson, 1997) compared to the large pelagic. However, the high ingestion rate of the squids (Jackson et al., 1998), combined with prey items (and hence, mercury concentration in the diet) were similar to the yellowfin tuna and could explain the higher mercury levels in this species. On the other hand, pelagic red crab *P. planipes* comprised a high percentage of the yellowfin tuna diet (Galván, 1988; Alatorre, 2007), and this crustacean could be an important source of mercury. However, a lower bioaccumulation of mercury can be expected, since pelagic red crab had low mercury contents (Fig. 2). Furthermore, pelagic red crabs should provide less mercury because their body is covered by achitinous exoskeleton that is hard to digest. Pelagic red crabs were analyzed whole; it is probable that there is an important accumulation of mercury in the exoskeleton of this crustacean, since the detoxification mechanisms of these invertebrates involve shedding the exoskeleton (Walker et al., 1996). Furthermore, mercury analysis of the pufferfish *L. lagocephalus* provided an interesting contrast with yellowfin tuna. The pufferfish belongs to the Tetraodontiae family and feeds on benthic crustaceans, planktonic crustaceans, squid and sepias (Tortonese, 1986). The low mercury levels in pufferfish muscle tissue could be due to a lower mercury input in *L. lagocephalus*; feeding could be based mainly on zooplanktonic species, which bioaccumulate low mercury concentrations (Tadiso et al., 2011). However, the low mercury value recorded for *L. lagocephalus* could also be due to mercury accumulation occurring in other tissues (liver, kidneys, and pancreas) and not in the analyzed muscle.

Several papers have examined possible mechanisms for the antagonistic effect between Hg and Se (Yang et al., 2008; Peterson et al., 2009; Khan and Wang, 2009). Khan and Wang (2009) proposed six pathways which have contributed to Hg–Se antagonism, and at the molecular level they are all based on the same mechanism: the formation of certain Hg–Se compounds witch different mobility, bioavailability, and affinity to the target sites. It is likely that more than one Se–Hg compound is involved for the Hg–Se antagonism. In the majority of species investigated here a molar excess of Se over Hg were reported in both fish and seafood. In other studies, a majority of species investigated also showed a molar excess of Se over Hg in both marine (Fang et al., 2011) and freshwater (Peterson et al., 2009). Despite the very small sample sizes for most species analysed, with the exception of yellowfin tuna, jumbo squid, and pelagic red crab, it was still possible to observe the positive correlation between Hg and Se previously reported for the tissues of marine mammals and the aquatic organisms in general (Plessi et al., 2001; Kaneko and Ralston, 2007; Elorriaga-Verplancken and Aurioles-Gamboa, 2008).

Kaneko and Ralston (2007) proposed an index to help identify fish species with low Hg levels and high Se content. Their selenium health benefit value (Se-HBV) index is calculated by considering both the absolute and the relative concentrations of Hg and Se on a molar basis in a given sample. Here, the Se-HBV exceeded 200 in pufferfish (298.4), and exceeded 60 in yellowfin tuna (64.5) and purple squid (63.5) (Table 2). The Se content measured in yellowfin tuna was among the highest across species, but the Se-HBV reported here is not high to other tuna studied. Fang et al. (2011) founded a Se-HBV index of 295.7 in yellowfin tuna from Taiwan was similar to those found by Kaneko and Ralston (2007) for this same tuna species in the Central Pacific close to Hawaii. The Se-HBV of yellowfin tuna reported here demonstrates that tuna and other large pelagic fish are a rich source of selenium.

Another major knowledge gap in the Hg–Se antagonism is that the underlying effects of Se chemical species, concentration, and administration method are poorly known. At the molecular level, both Hg^{2+} and MeHg are toxic. The differences lie in the uptake route (MeHg can readily cross the blood–brain barrier, and inorganic Hg^{2+} does not) and in the bindings affinity (Hg^{2+} has a much stronger binding affinity toward –SH sites in biological systems than $MeHg^{+}$) (Khan and Wang, 2009). Therefore, should Hg^{2+} be present in the brain (either by MeHg demetylation or by Hg^{0} oxidation), it would be much more neurotoxic than MeHg. In addition, the toxicity of MeHg could also be attributed to the CH_3 radicals produced by homolysis or to Se deficiency (Khan and Wang, 2009). The validity and relative importance of these different modes of toxic action remain to be determined. There is evidence that dietary Se could not influence the ingested MeHg bioavailability via biokinetic modification. It was clear that Se interacted in an antagonistic way with Hg (II) rather than with MeHg (Dang and Wang, 2011). On the other hand, it is well recognized that selenium has the capacity to reduce the toxicity of inorganic Hg, forming a complex with equal proportions of the two elements (Elorriaga-Verplancken and Aurioles-Gamboa, 2008). Mercury could bind with selenium to form insoluble mercury selenides at molecular level. The inert complexes resulted in a decreased bioavailability and less toxicity of both Hg and Se to organism (Cuvin-Aralar and Furness, 1991), since they may be less solubilised from the prey and absorbed by the predator's intestine. The formation of these solids is the final step in the biochemical process of detoxification and may be another reason to explain that selenium decreased mercury bioavailability.

In regards to the health of the fish themselves, as well as their potential risk of toxicity to free living animals and humans that consume fish containing mercury, *T. albacares* and analyzed prey (*V. lucetia*, *L. lagocephalus, D. gigas*, *T. rhombus*, *S. oualaniensis*, *P. planipes*) did not exceed the Mexican standards of 1 μg Hg g^{-1} for large fish, and 0.5 μg Hg g^{-1} for molluscs (Secretaría de Salud, 2009). Moreover, these values were low and do not come close to the criterion of 0.3 μg MeHg g^{-1} established by the U.S. Environmental Protection Agency (EPA) for eatable fish tissue (U.S. Environmental Protection Agency, 2001). On the other hand, Se body burden was elevated significantly, which were still within the reported values in field studies (Peterson et al., 2009) and lower than the toxic effect threshold of fish (1.0 μg g^{-1}) (Lemly, 1993). Finally, the presence of selenium in high proportion over mercury gives benefits to the consumer's health, and is also associated with an increase in antioxidant values, which help immune system functions and have cancer-fighting effects. It also has a protection effect against mercury toxicity. Future studies of joint mercury and selenium accumulation can help understand their interaction and the benefit that selenium represents as an antagonistic element in animals and humans.

5. Conclusions

In waters off the western coast of Baja California Sur, as well as on its eastern side, pelagic fish species are abundant and are caught by Mexican commercial fisheries. The meat fish is greatly appreciated for being tender and delicious and for the beneficial influence of its nutrients: high-quality protein, ω-3 fatty acids, vitamins, and minerals. However, eating large predatory fish (e.g., shark, swordfish, marlin, and tuna) may place the individual at risk of serious illness due to their high levels of metals. It has been show here that, the yellowfin tuna *T. albacares* and its species prey off the western coast of Baja California Sur contained mercury, showing that they can accumulate this metal and be a source of mercury to the predator. All mercury values not exceeded the 1.0 $\mu g\ g^{-1}$ Norma Mexican guideline. Selenium, as expected, was high over Hg in all species. In all species studied there was a molar excess of Se over Hg, suggesting a positive Se-HBV in relation to Hg. These data concerning levels of Hg, Se, and Se/Hg molar rations in commercial marine fish are important aspects that should be considered in regards to safety of marine product consumption.

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