#### RESEARCH ARTICLE



# Mercury (Hg) and selenium (Se) content in the shark Mustelus henlei (Triakidae) in the northern Mexican Pacific

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#### Abstract

Mercury and selenium were assessed in *Mustelus henlei*, which is a carnivorous predatory shark that is important for the coastal communities of the northern Mexican Pacific (NMP). Sixty-two individuals were sampled; muscle and liver were isolated and analyzed by atomic absorption spectrophotometry. The mean Hg concentrations (wet weight) obtained for muscle (0.08 ± 0.10 µg  $g^{-1}$ ) and liver  $(0.09 \pm 0.26 \,\mu g \,g^{-1})$  were below the allowed limits (< 1.0  $\mu g \,g^{-1}$  Hg). The average Se concentration was  $0.03 \pm 0.01 \,\mu g \,g^{-1}$  in muscle and 0.13  $\pm$  0.05 μg g<sup>-1</sup> in liver. The Se/Hg molar ratio of muscle was 1.83; however, the selenium health benefit value (HBV<sub>Se</sub>) was of 0.08. We calculated that an adult man (70 kg), an adult woman (60 kg), and a child (16 kg) could consume 1595, 838, and 223 g/week of M. henlei muscle, respectively, without risks to health. In conclusion, the concentrations and molar ratio of Hg and Se in M. henlei muscle mean that consumption of this shark's meat does not represent neither a benefit nor a public health risk.

Keywords Elasmobranchs · Chemical antagonism · Metal(oid)s · Spectrophotometry · Human health

# Introduction

Mercury (Hg) occurs in organic and inorganic forms in the marine environment. The transformation of Hg between these two forms can have major effects on the bioaccessibility, mobility, volatility, and solubility of this metal through biological or chemical processes (Storelli et al. [2002\)](#page-8-0). Briefly, Hg accumulates rapidly and mainly in its methylated form  $(CH<sub>3</sub>Hg)$ , which passage across cell membranes; moreover, its high affinity for the sulfhydryl groups of protein and enzymes, its

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half-life, and its tendency to bioaccumulate from one trophic level to the next and increasing its concentration throughout the trophic web makes it a hazardous substance to human health and the environment (Gray [2002;](#page-7-0) Storelli et al. [2002\)](#page-8-0). Thus, to protect public health, a maximum permissible limit has been established in marine products for human consumption in Mexico. For fish, the level limit for total Hg (NOM-027-SSA1-1993 [1995](#page-8-0)) is 1.0  $\mu$ g g<sup>-1</sup> (wet weight) and for methyl-Hg (CH<sub>3</sub>Hg), the value is 0.5 μg g<sup>-1</sup> (NOM-242-SSA1-2009 [2011\)](#page-8-0).

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On the other hand, selenium (Se) is a metalloid essential for metabolism; however, in elevated concentrations, Se can be harmful to human health (Plant et al. [2001](#page-8-0)). It is well known that Se can counteract Hg toxicity. Selenium does not decrease Hg concentrations, but it neutralizes the effects of Hg in the body when both elements occur together. A Se:Hg molar ratio above 1:1 is considered protective against adverse mercury effects (Kaneko and Ralston [2007](#page-8-0); Burger et al. [2012](#page-7-0)). Selenium might contribute to the CH<sub>3</sub>Hg demethylation process in organisms through selenocysteine; Hg might be transformed to inorganic Hg that can be excreted in an easier and simpler manner through the urinary and gastrointestinal tracts (Mann and Truswell [2002;](#page-8-0) Havelková et al. [2008\)](#page-8-0). There is no regulation in Mexico stating allowable Se limits; however, other countries have established limits of 6.5 μg  $g^{-1}$  dry weight (USA) (Skorupa et al. [1996\)](#page-8-0) and 1.0  $\mu$ g g<sup>-1</sup> dry weight (Australia) (Nauen [1983\)](#page-8-0) to guarantee public well-being.

The main pathway for exposure to essential and nonessential elements is through food; therefore, products that are frequently consumed by humans should be monitored. Fish have been identified as a source of Hg and Se exposure in humans (Squadrone et al. [2014\)](#page-8-0), particularly fish at high trophic levels such as elasmobranchs (sharks and rays). Actually, Mexico is one of the most important countries in terms of fisheries production and of elasmobranch catches (Ramírez-Amaro et al. [2013](#page-8-0)). In addition to providing a food resource in Mexico, the elasmobranch fishery creates numerous jobs for the coastal communities of Mexico (Bizzarro et al. [2009](#page-7-0)). The Triakidae family includes the brown smoothhound shark Mustelus henlei, an abundant species in the northern Mexican Pacific (NMP) which is distributed in temperate and tropical waters at depths ranging from the shallow intertidal to 200 m with a geographic range spanning Coos Bay, Oregon (USA), to Peru and Ecuador including the Gulf of California. However, this species is considered to occur primarily in the northern Pacific (Chabot et al. [2015\)](#page-7-0). M. henlei constitutes a commercial resource in Mexico (Rodríguez-Romero et al. [2013\)](#page-8-0). This shark has been classified as K-type strategists, because they display slow growth, long gestation times, low fecundity, and late age at maturity (Holden [1974\)](#page-8-0). These biological characteristics make them susceptible to overfishing and to exposure to toxic elements.

Due to its toxicity, persistence, and accumulation capacity, it is important to investigate Hg and Se levels in marine ecosystems and in commercially important species such as the brown smooth-hound shark *M. henlei*. Moreover, Hg and Se levels should be evaluated jointly to understand in an integrated manner the antagonistic relationship between these elements, and to verify the toxicity of Hg in products consumed by humans. Hypothetically, sharks are considered long-lived top predators, and we expected to find Hg values in M. henlei above the permissible limits allowed by Official Mexican Standards (> 1.0 μg  $g^{-1}$ ), but with a molar ratio of Se:Hg ≥ 1. Actually, Hg

and Se levels in M. henlei are unknown, so the purposes of the present study were to assess whether Hg and Se concentrations found in M. henlei are within allowable limits set by Mexican and international regulations, and to assess the Se (selenium health benefit value  $(HBV_{Se})$ ) benefit to public health from consumption of this shark's meat. In addition, Hg and Se concentrations in liver were also evaluated.

# Materials and methods

#### Field sampling

Sixty-two specimens of brown smooth-hound shark M. henlei were collected from eight sites in the northern Mexican Pacific Ocean (NMP) (Fig. [1](#page-2-0)), during 2015 (June, July, August, and October), 2016 (April, June, July, and August), and 2017 (July and August). Sharks were captured using shrimp trawl nets with  $2\frac{3}{4}$ -in. mesh size and bottom-set gillnets with 3.5- to 6in. mesh size placed at selected sites in the NMP. Total length  $(T<sub>L</sub>)$  was measured before dissection, and sex and maturity state (juvenile and adult) were recorded. Males of  $T_L$  > 64 cm and females of  $T_L > 68$  were considered mature (Silva-Santos [2012](#page-8-0)). Muscle (from dorsal section) and liver samples  $($   $\sim$  5 g) were obtained from each specimen and stored in polyethylene bags at − 20 °C until processing.

#### Chemical analysis

Muscle and liver samples were weighed and lyophilized at  $-35$  °C and  $100 \times 10^{-3}$  mbar during 72 h; samples were then ground and homogenized using an agate mortar and pestle. Samples  $({\sim}0.25 \text{ g})$  were pre-digested overnight with 5 mL of nitric acid  $(HNO<sub>3</sub>)$  in a closed Teflon container (Savillex). Digestion was performed using hot plates (Barnstead) during 3 h at 120 °C. Digested samples were then diluted to 25 mL with Milli-Q water. Hg concentration was measured using a cold vapor spectrophotometer (CV-AAS) with stannous chloride  $(SnCl<sub>2</sub>)$  as reducing agent and a 253.5-nm cathode lamp, whereas Se concentration was measured with a 196-nm cathode lamp and hydride generation (Varian Model VGA-77), using NaBH4 and an air-acetylene flame. Before Se analysis, 1 mL of nitric acid (trace metal grade) was added to 7 mL of digested sample and placed in a polyethylene container in a water bath at 120 °C. Hg and Se concentrations are expressed as  $\mu$ g g<sup>-1</sup> wet weight. Accuracy of the analyses and results was validated by using blanks and two certified reference materials (DORM-3 fish protein and DOLT-4 dogfish liver). The average recovery for Hg was 83.8% in the DORM-3 and 91.5% in the DOLT-4; and for Se, was 83.0% in the DOLT-4.

<span id="page-2-0"></span>Fig. 1 Location of sites (black circle) where Mustelus henlei specimens were obtained in the northern Mexican Pacific. BC Baja California, BCS Baja California Sur, SIN Sinaloa, SON Sonora



# Statistical analysis

Data normality was analyzed statistically using Kolmogorov-Smirnov and Levene's tests (Zar [1999\)](#page-9-0). Hg concentrations did not display a normal distribution (muscle: K-S,  $d =$ 0.3076,  $p < 0.01$ ,  $n = 62$ ; liver: K-S,  $d = 0.22691$ ,  $p < 0.01$ ,  $n = 62$ ), whereas Se concentrations showed normality (muscle: K-S,  $d = 0.13425$ ,  $p > 0.20$ ,  $n = 62$ ; liver: K-S,  $d = 0.09402$ ,  $p > 0.20$ ,  $n = 62$ ). Mann-Whitney's U test and Spearman's correlations were applied to Hg data, whereas Student's  $t$  test and Pearson's correlation were applied to Se data. Statistical analysis was performed with STATISTICAL software.

#### Se/Hg molar ratio

The Se/Hg molar ratio, mean, and standard deviation were calculated for each shark. The concentrations, measured as  $\mu$ g g<sup>-1</sup>, were converted to μmol kg<sup>-1</sup> and the Se/Hg molar ratio calculated from molar mass of Hg (200.59 g mol<sup>-1</sup>) and Se (78.96 g mol<sup>-1</sup>).

# Health benefits

The  $HBV_{Se}$  was calculated as follows (Ralston et al. [2016\)](#page-8-0):

$$
HBVSe = \left(\frac{(Se-Hg)}{Se}\right) \times (Se + Hg)
$$

This equation includes Hg and Se molar concentrations. A positive  $HBV_{Se}$  indicates a health benefit, but a negative result of  $HBV_{Se}$  indicates that the health risk occurs.

#### Health risk assessment

The maximum consumption of fish per week (MCFW) of Hg was calculated using the following formula:

$$
MCFW = \frac{PTIW}{[Hg]j}
$$

where PTIW is the provisional tolerable intake per week (4.0 μg kg<sup>-1</sup> body weight week<sup>-1</sup> for men; 2.45 μg<sup>-1</sup> kg<sup>-1</sup> body weight week−<sup>1</sup> for pregnant women, lactating women, or children; JECFA [2010\)](#page-8-0) and [Hg]j is the M. henlei Hg concentration (μg  $g^{-1}$ ). MCFW is expressed in g of fish intake week<sup>-1</sup> per capita (kg). Average weights of 70 kg (adult men), 60 kg (adult women), and 16 kg (children) were included in the analysis.

Considering that the contribution of methylmercury to total mercury is commonly 80–100% in fish, a conversion of mercury to methylmercury was realized applying the 90% (EFSA [2012\)](#page-7-0). Likewise, the MCFW was established with the PTWI for methylmercury (1.6  $\mu$ g kg<sup>-1</sup> wet weight) (EFSA [2012\)](#page-7-0). For women and children, a proportional PTWI (2.45 to 0.98  $\mu$ g<sup>-1</sup> kg<sup>-1</sup> body weight week<sup>-1</sup>) was applied according to the JECFA ([2010](#page-8-0)).

#### **Results**

Tissue samples (muscle and liver) from 62 sharks were obtained (12 males, 41 females, 9 uncategorized), comprising 31 juveniles, 22 adults, and 9 uncategorized. The sharks ranged in length from 43.5 to 102.7 cm (mean =  $67.8 \pm 14.4$  cm). Males and females reach sexual maturity at 64 cm and 68 cm, respectively (Silva-Santos [2012](#page-8-0)). Unfortunately, some individuals were considered as uncategorized due to sex and size were not recorded. These individuals were not included in the specific analysis by male/female and juveniles/adults, but these data were included in the general average of Hg and Se.

## Mercury and selenium in muscle and liver, influence of sex and size

The mean Hg concentration ( $\mu$ g g<sup>-1</sup>) for *M. henlei* was 0.08 ± 0.11 in muscle (0.01–0.68,  $n = 62$ ) and  $0.09 \pm 0.26$  in liver  $(0.01-2.02, n = 62)$ . Se concentrations were obtained in muscle  $(0.03 \pm 0.02; 0.01 - 0.06, n = 62)$  and liver  $(0.13 \pm 0.05;$ 0.02–0.26,  $n = 62$ ).

There were no statistically significant differences in Hg concentration between males (muscle =  $0.11 \pm 0.19$ ; liver =  $0.06 \pm 0.06$ ) and females (muscle =  $0.07 \pm 0.06$ ; liver = 0.05  $\pm 0.04$ ) for muscle (U = 193, p > 0.05) or liver (U = 189,  $p > 0.05$ ) (Table 1). Similarly, Se values of females (muscle =  $0.03 \pm 0.02$ ; liver =  $0.07 \pm 0.06$ ) and males (muscle =  $0.03 \pm 0.03$ ) 0.01; liver =  $0.14 \pm 0.07$ ) were not significantly different (muscle:  $t = 1.13$ ,  $p > 0.05$ ; liver:  $t = 1.74$ ,  $p > 0.05$ ) (Table 1).

Mean Hg concentrations of adults  $(0.12 \pm 0.15)$  and juveniles  $(0.05 \pm 0.04)$  were significantly different for muscle  $(p < 0.05)$  but not for liver (juveniles  $0.05 \pm 0.04$ ; adults  $0.07 \pm 0.06$ ;  $U = 224$ ,  $p > 0.05$ ). Se concentrations were not significantly different between adults and juveniles for muscle

(adults  $0.02 \pm 0.01$ , juveniles  $0.03 \pm 0.02$ ) or liver (adults 0.02)  $\pm 0.01$ ; juveniles  $0.03 \pm 0.02$ ) (Table 1).

Correlations between size  $(T<sub>L</sub>)$  and Hg concentrations were significantly positive for muscle ( $r_s = 0.35$ ,  $p < 0.05$ ) and liver  $(r<sub>s</sub> = 0.27, p < 0.05)$  (Fig. [2a](#page-4-0)). Se was not significantly ( $p > 0.05$ ) associated with  $T<sub>L</sub>$  (muscle  $r<sup>2</sup> = 0.01$ ; liver  $r<sup>2</sup> =$ 0.12) (Fig. [2b\)](#page-4-0).

#### Toxicological and health benefit assessment

The calculated amount of shark filet that a man (70 kg) could consume safely per week was 3590 g; however, a consumption of 412 g is recommended because an individual shark presented Hg concentrations above 1.0  $\mu$ g g<sup>-1</sup>. Restrictions are more rigorous for women and children, especially with the estimation of  $CH<sub>3</sub>Hg$  (Table [2\)](#page-4-0).

The molar ratio of liver  $(Se/Hg_{(liver)} = 7.78)$  was higher than that of muscle (Se/Hg<sub>(muscle</sub>) = 1.83); however, considering the HBV<sub>Se</sub> value obtained for muscle tissue, there was not a high Se benefit (Table [3](#page-5-0)), whereas hepatic tissue showed a more positive  $HBV_{Se}$  value.

#### **Discussion**

#### Mercury and selenium: tissue distribution and influence of sex and size

This is the first study on the Se/Hg relationship in M. henlei in the northern Mexican Pacific. Hg concentrations found in this species were below the maximum Hg limit established by Mexican norms (NOM ≥ 1.0 µg  $g^{-1}$  on wet weight basis). These results are consistent with the general pattern reported for congeneric species (e.g., M. griseus, M. schimitti,

Table 1 Hg and Se concentrations ( $\mu$ g g<sup>-1</sup> ww) in muscle and liver of males, females, juveniles, and adults of *M. henlei* 

Tissue	Sex/maturity state	$n^*$	Hg		<b>Se</b>		
			Min-Max	$\overline{x}$ ± SD	Min-Max	$\overline{x}$ ± SD	
Muscle	Male	12	$0.01 - 0.68$	$0.11 \pm 0.19$	$0.02 - 0.05$	$0.03 \pm 0.01$	
	Female	41	$0.01 - 0.32$	$0.07 \pm 0.06$	$0.01 - 0.06$	$0.03 \pm 0.02$	
Liver	Male	12	$0.01 - 0.23$	$0.06 \pm 0.06$	$0.04 - 0.26$	$0.14 \pm 0.07$	
	Female	41	$0.01 - 0.22$	$0.05 \pm 0.04$	$0.02 - 0.21$	$0.07 \pm 0.06$	
Muscle	Adult	22	$0.01 - 0.68$	$0.12 \pm 0.15$	$0.01 - 0.04$	$0.02 \pm 0.01$	
	Juvenile	31	$0.01 - 0.24$	$0.05 \pm 0.04$	$0.02 - 0.06$	$0.03 \pm 0.02$	
Liver	Adult	22	$0.01 - 0.23$	$0.07 \pm 0.06$	$0.02 - 0.04$	$0.02 \pm 0.01$	
	Juvenile	31	$0.01 - 0.14$	$0.06 \pm 0.03$	$0.02 - 0.26$	$0.03 \pm 0.02$	

Min minimum, Max maximum,  $\overline{x}$  mean, SD standard deviation

\*Nine uncategorized individuals were not included

n Sample size

<span id="page-4-0"></span>

Fig. 2 Correlation between total length  $(T_L)$  and mercury (a) and selenium (b) concentrations in M. henlei (muscle and liver)

M. norrisi) in different regions, including the western coast of Baja California Sur, Mexico (Espinoza-García [2016\)](#page-7-0) (Table [4](#page-5-0)). This has been mainly attributed to feeding and life habits and other factors such as metabolic and growth rates of the species (Andersen and Depledge [1997\)](#page-7-0). Piscivore species occupying high trophic levels show significantly higher Hg concentrations than consumers of crustaceans or cephalopods (Storelli and Marcotrigiano [2000](#page-8-0); Escobar-Sánchez et al. [2016\)](#page-7-0). Espinoza et al. [\(2015\)](#page-7-0) found that the diets of immature individuals of M. henlei in the Pacific coast of Costa Rica consisted of larger proportions of invertebrates (e.g., shrimp, stomatopods, and polychaetes), while teleosts were more important (in terms of biomass, frequency, and abundance) for adults. Conversely, Amariles et al. [\(2017\)](#page-7-0) in the coast of the Colombian Pacific found that this species fed almost exclusively on teleosts. However, the diet of *M. henlei* in Mexican waters includes crustaceans, mainly (index of relative importance, 81.4%) the pelagic red crab Pleuroncodes planipes (Rodríguez-Romero et al. [2013\)](#page-8-0). Therefore, predation upon low trophic level preys such as crustaceans could lead to lower Hg levels in *M. henlei* that in top predators.

In some locations (e.g., Japan or South Africa), high Hg levels ( $\geq 1.0 \mu g g^{-1}$ ) have been observed in *Mustelus* species such as *M. mustelus* and *M. manazo* (Table [4\)](#page-5-0); these high values were attributed to differences in size and biological differences between sexes (habits, size, etc.) (Pethybridge et al. [2010](#page-8-0)). Some authors have reported that intraspecific differences in Hg concentrations between males and females could be caused by factors such as energetic requirements, maturity conditions, Hg deposition, and Hg transfer from females to embryos (Lyle [1986](#page-8-0); Frías-Espericueta et al. [2015\)](#page-7-0). It has even been considered that in some species such as M. mustelus, the growth rate of males is slower than that of females, and this could imply that the muscle tissue of males has greater Hg concentrations than that of females (Bosch et al. [2013\)](#page-7-0). However, in our study, no statistical differences were found in the Hg concentrations of the two sexes, which indicate a lack of sexual segregation; both sexes could share the same biological and ecological characteristics as habitat and sources of elements, migratory routes, feeding types, growth rates, etc. (Núñez-Nogueira et al. [1998](#page-8-0)). No differences have been found between M. henlei males and females in feeding habits or behavior in the NMP (Rodríguez-Romero et al. [2013\)](#page-8-0), which could explain the similar Hg concentrations found in this study for both sexes and tissue types.

Intraspecific variations have also been associated with length, weight, age, and sexual maturity (Wheeler [1996](#page-9-0)). In this study, a significantly positive correlation was found between  $T_{\text{L}}$  and Hg concentrations in muscle and liver, which indicates that the concentration level could increase with size, as has been reported for other sharks, such as Galeocerdo cuvier, Carcharhinus albimarginatus, C. plumbeus, and C. leucas (Endo et al. [2008\)](#page-7-0). However, more adult specimens

**Table 2** Amount of *M. henlei* meat (g) that could be ingested per week. [Hg] and [CH<sub>3</sub>Hg] are given as average

Shark category	[Hg]	Meat ingestion (g) per week			[MeHg]	Meat ingestion (g) per week		
		Man $(70 \text{ kg})$	Woman $(60 \text{ kg})$	Child $(16 \text{ kg})$		Man $(70 \text{ kg})$	Woman $(60 \text{ kg})$	Child $(16 \text{ kg})$
Overall	0.08	3590	1885	503	0.07	1595	838	223
Males	0.11	2545	1336	356	0.11	1018	535	143
Females	0.07	4000	2100	560	0.07	1600	840	224
Juveniles	0.05	5600	2940	784	0.05	2240	1176	314
Adults	0.12	2333	1225	327	0.12	933	490	131
Maximum value	$0.68*$	412	216	58	0.61	183	838	223

\*Maximum value

<span id="page-5-0"></span>Table 3 Molar ratio of Se and Hg in selected tissues of M. henlei, including the health benefit value of selenium (HBV<sub>Se</sub>)

Tissue [Hg]		$[Se]$ $\mu$ mol Hg $\mu$ mol Se	Se/ Ηg	$HBV_{Se}$
Liver		Muscle $0.08 \pm 0.11$ $0.03$ $0.34 \pm 0.32$ $0.38 \pm 0.17$ 1.83 $0.09 \pm 0.26$ 0.13 $0.27 \pm 0.22$ 0.34 $\pm 0.67$ 7.78		0.08 $-1.60$

should be studied to explain this trend, as it has been reported that adults tend to have a slow metabolism and, therefore, they would need more time to metabolize Hg, which decreases excretion rate and results in greater Hg accumulation in tissues. Larger animals feed on larger preys, which would also lead to a greater quantity of Hg in consumers (de Pinho et al. [2002;](#page-7-0) Gutiérrez-Mejía et al. [2009\)](#page-7-0).

Selenium concentrations found in M. henlei muscle and liver were under the allowable limits established for human

Table 4 Hg and Se concentrations in muscle and liver of sharks from the genus Mustelus at different geographic locations. Values are expressed as μg  $g^{-1}$  (wet weight).  $\delta$  = males,  $\mathcal{Q}$  = females

Shark species	Country	[Hg] muscle	[Hg] liver	[Se] muscle	[Se] liver	Author
M. antarcticus	Australia	$0.75 \pm 0.27$	$\overline{\phantom{0}}$		$\qquad \qquad$	Ratkowsky et al. (1975)
M. canis	France	0.53	$\overline{\phantom{0}}$	$\overline{\phantom{a}}$	÷	Cumont et al. (1975)
M. antarcticus	Australia	$0.07 \pm 3.00$				Walker (1976)
M. antarcticus	Australia	0.5	$\overline{\phantom{0}}$	$\overline{\phantom{0}}$	$\overline{\phantom{0}}$	Bloom and Ayling (1977)
M. antarcticus	Australia	$1.18 \pm 0.45$		$0.35 \pm 0.19$	$\equiv$	Glover (1979)
M. griseus	Japan	0.03		0.31		Ueda and Takeda (1983)
М. тапаго	Japan	0.3		0.29	$\overline{\phantom{0}}$	Ueda and Takeda (1983)
M. schmitti	Argentina	$0.46 \pm 0.17$			$\overline{\phantom{0}}$	Perez et al. (1985)
M. schmitti	Argentina	$0.85 \pm 0.42$			$\overline{\phantom{0}}$	Marcovecchio et al. (1986)
M. schmitti	Argentina	$0.03 \pm 3.26$	$0.00 \pm 2.31$		$\equiv$	Marcovecchio et al. (1991)
M. schmitti	Argentina	$0.45 \pm 0.30$				Scapini et al. (1993)
M. higmani	<b>Brazil</b>	0.05			—	Lacerda et al. $(2000)$
M. higmani	South America	$0.71 \pm 0.41$	$\overline{\phantom{0}}$	$\overline{\phantom{0}}$	$\overline{\phantom{0}}$	Mol et al. (2001)
M. canis	South America	0.09		$\overline{\phantom{0}}$	$\qquad \qquad -$	Mol et al. (2001)
M. norrisi	<b>Brazil</b>	$0.36 \pm 0.28$			$\overline{\phantom{0}}$	de Pinho et al. $(2002)$
M. canis	<b>Brazil</b>	$0.41\pm0.35$	<u>—</u>	$\overline{\phantom{0}}$	$\overline{\phantom{0}}$	de Pinho et al. $(2002)$
M. norrisi	<b>USA</b>	$1.20 \pm 1.20$		$\overline{\phantom{a}}$	$\equiv$	Adams et al. (2003)
M. asterias	<b>Brazil</b>	$1.7 \pm 3.1$			$\overline{\phantom{0}}$	Domi et al. (2005)
M. schmitti	Argentina	$0.33 \pm 0.20$				De Marco et al. $(2006)$
M. mustelus	Mediterranean Sea	$0.39 \pm 0.37$				Kousteni et al. (2006)
M. henlei	Mexico	$0.18 \pm 0.1$			$\overline{\phantom{0}}$	García-Hernández et al. (2007)
M. mustelus	Italy	0.16				Storelli et al. (2011)
M. mustelus	South Africa	0.03		0.95	$\equiv$	Zaera and Johnsen (2011)
M. albipinnis	Mexico	$0.19 \pm 0.69$	$0.05 \pm 0.28$		$\equiv$	Hurtado-Banda et al. (2012)
M. mustelus	South Africa	$0.74 \pm 0.20$ ( $\circledcirc$ )	$\equiv$		$\overline{\phantom{0}}$	Bosch et al. (2013)
M. mustelus	South Africa	$1.37 \pm 0.05$ ( $\circlearrowleft$ )				Bosch et al. (2013)
М. тапаго	Japan	$0.78 \pm 0.46$ ( $\circledcirc$ )	$0.61 \pm 0.75$ ( $\circledcirc$ )	÷	$\overline{\phantom{0}}$	Endo et al. (2013)
M. manazo	Japan	$1.15 \pm 0.57$ ( $\circled{)}$ )	$1.17 \pm 1.73$ ( $\circlearrowleft$ )			Endo et al. (2013)
M. canis	England	$3.3 \pm 2.1$				Taylor et al. $(2014)$
M. mustelus	South Africa	$0.96 \pm 0.69$	$\equiv$	$0.70 \pm 0.44$	$\qquad \qquad -$	Bosch et al. (2016)
M. henlei	Mexico	$0.34 \pm 0.11$	$0.11 \pm 0.09$		$\equiv$	Espinoza-García (2016)
M. manazo	Japan	$1.18 \pm 0.61$ ( $\circledcirc$ )	$2.08 \pm 2.10$		$\overline{\phantom{0}}$	Endo et al. (2017)
M. manazo	Japan	$0.81 \pm 0.51$ (3)	$0.91 \pm 1.09$			Endo et al. (2017)
M. henlei	Costa Rica	$0.16 \pm 0.9$	$\overline{\phantom{0}}$			Sandoval-Herrera et al. (2016)
M. henlei	Mexico	$0.08 \pm 0.11$	$0.09 \pm 0.26$	$0.03 \pm 0.01$	$0.13 \pm 0.05$	This study

consumption by the Health Department of Australia (1.0 μg g<sup>-1</sup> ww) (Nauen [1983](#page-8-0)) and of the USA (6.5 μg g<sup>-1</sup> dry weight) (Skorupa et al. [1996](#page-8-0)). Based on this, values obtained for M. henlei muscle and liver in the NMP do not represent a risk of intoxication from Se.

Studies on Se presence in sharks are scarce in Mexico. However, in other regions, Se concentrations have been assessed in Mustelus species, such as M. griseus (Japan) and M. mustelus (South Africa), where it was found that Se values were higher than Hg values in muscle tissue (Ueda and Takeda [1983;](#page-9-0) Zaera and Johnsen [2011](#page-9-0)). It should be mentioned that this is not a general pattern for the Mustelus genus, as it was reported that Se values were lower than Hg concentrations in M. manazo and M. mustelus (Ueda and Takeda [1983](#page-9-0); Bosch et al. [2016\)](#page-7-0); this could be due to factors such as element bioavailability in ecosystems and stage of organisms. It has been reported that there are greater quantities of Se in the liver because that is where Hg detoxification occurs (Branco et al.  $2007$ ), which would explain that in *M. henlei*, the greatest Se concentrations were found in liver tissue. Moreover, demethylation and Hg accumulation occur in the liver through the effect of the selenoproteins of glutathione (GSH), that contribute to eliminate Hg by excreting it in the bile as cysteinemercury (Patrick [2002;](#page-8-0) Branco et al. [2007\)](#page-7-0). That is, Se tends to be found in greater concentrations in the liver because it dominates in the competition for space in the liver; the opposite occurs in muscle, where Hg is more dominant due to its affinity with muscular tissue and with the thiol groups of proteins (Lacerda et al. [2000](#page-8-0); Raymond and Ralston [2004](#page-8-0)). Despite the possibility of this affinity and even though Se concentrations in muscle are lower than those of liver, in this study, there were no significant differences of Se concentrations between the two tissues. There were no significant differences in Se values between males and females, or between juveniles and adults for the two analyzed tissues, which could be due to the same intraspecific factors that influenced Hg concentrations, such as similar type of food, habitat, and probably the same availability of both elements.

# Toxicological and health benefit assessment—Se:Hg molar ratio

According the concentrations found here of Hg in M. henlei, such Hg values should not represent a risk to human health (NOM-031-SSA1-1993; NOM-0242-SSA1-2009). However, as a precautionary measure, we recommend that an adult man (70 kg) should consume only up to 183 g per week of M. henlei meat to reduce possible risks; a specimen with Hg concentration below 1.0 μg  $g^{-1}$  was found in this study. Women (60 kg) can consume up to 96 g of  $M$ . henlei meat, and children (16 kg) can consume up to 26 g per week. Although these recommendations can appear strict, the US-EPA (United States Environmental Protection Agency) has

stated that rigorous restrictions are meant to protect human health. However, concentrations as well as the time of exposure should be taken into account, to establish whether exposure was acute or chronic.

The Se benefit value measured through the  $HBV_{Se}$  index was very low in muscle compare with other predators as the silky shark Carcharhinus falciformis (HBV $_{\text{Se}}$  = 52.3; Bodin et al. [2017\)](#page-7-0) or dolphinfish Coryphaena hippurus (HBV $_{\rm Se}$ = 1.77; Vega-Sánchez et al. [2019](#page-9-0)) because Hg concentrations were higher than Se concentrations. The opposite  $(Se > Hg)$ was found in *M. henlei* liver tissue, indicating a benefit provided by a greater quantity of Se compared with Hg in the liver tissue. This was also previously reported for the shark Prionace glauca, based on the Se/Hg molar ratio (Escobar-Sánchez et al. [2011\)](#page-7-0). Some shark species such as Sphyrna zygaena have been reported to display a greater Se molar proportion compared with Hg (Escobar-Sánchez et al. [2010\)](#page-7-0), which in addition to neutralizing the effects of Hg could allow the animal to have enough Se for physiological processes. Considering the Hg and Se values obtained in the present study, which are below established regulations, there is no risk of intoxication caused by these elements from the consumption of M. henlei muscle, but given the low Se values found, there is no benefit to health from the consumption of this marine product.

# Conclusions

This is the first study on the relationship between Hg and Se in M. henlei in the world. Low Hg concentrations in M. henlei could be attributed to feeding habits and own specific parameters of the species such as a relatively low metabolic and growth rates or life habits (e.g., reproductive mode, habitats). A positive and significant  $(p < 0.05)$  correlation was observed between Hg in muscle and total length, with Hg concentration increasing with size. There were no significant differences for the Hg and Se concentrations between males and females, so the two sexes could be sharing the same habitat, feeding on the same resources, using the same migratory routes, with no relevant differences influenced by the dissimilarities in the growth rate, metabolism, or reproduction between sexes.

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