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Baseline

Total mercury and selenium levels in commercial shrimp along the Pacific coast of Mexico

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A R T I C L E I N F O

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A B S T R A C T

The present study analyzed the content of total mercury (THg) and selenium (Se) in the muscle of shrimp collected from local markets in the 11 Pacific coastal states of Mexico. Methylmercury (MeHg) concentration, Se:Hg ratio, health benefits value from selenium consumption (HBV_{Se}) and the permissible weekly consumption were estimated to assess the health risk to consumers. All THg and Se concentrations were below the maximum permissible limits. All hazard quotient (HQ) values were <1, however in Hermosillo, Culiacán and Guadalajara, the Se:Hg ratio and HBV_{Se} were <1 and negative, due to the low concentrations of Se. As a general conclusion, there is no risk nor benefit from the consumption of shrimp from the Pacific coast of Mexico due to its Hg and Se content.

Among the most toxic elements, mercury (Hg) occupies one of the first places. It is non-essential for human life, with methylmercury (MeHg) being its most toxic and bioaccumulative form (Ruelas-Inzunza et al., 2013). This metal enters the atmosphere and aquatic ecosystems as a result of natural processes such as volcanic activities and soil erosion and by industrial processes such as mining, combustion of petroleum derivatives and agriculture (Zhang and Wong, 2007). This metal is able to cross the blood-brain and placental membranes and may damage the central and peripheral nervous systems of adults, children, and fetuses. Furthermore, mercury may negatively affect the human immune and reproductive systems (Abdelouahab et al., 2008).

The main route of human exposure to Hg is through the consumption of organisms derived from fisheries (WHO, 2007), because Hg bioaccumulates and biomagnifies across aquatic food webs; and top predators tend to have the highest Hg concentrations and in turn represent a human health risk (Maz-Courrau et al., 2012). Shrimp, despite not being top predators, have a high consumption in coastal zones of Mexico (Delgado-Alvarez et al., 2015), which could put at risk people who consume these organisms.

On the other hand, selenium (Se) is an essential element for human life; functions such as the formation of selenoproteins and thyroid hormones, as well as antioxidant functions are attributed to this element (Mehdi et al., 2013). It has been shown that Se has the ability to mitigate the Hg toxic effects in humans, known as antagonism. According to Ralston and Raymond (2010) and Burger and Gochfeld (2013), there must be a Se:Hg molar ratio higher than 1; in this context, the protective effect of Se against Hg toxicity may be present and the Se bioavailability is not affected to perform its normal functions.

In Mexico, most of the studies of Hg and its health risk are regarding organisms captured directly through fishing, there is only one study with

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shrimp from markets, which was carried out by Reimer and Reimer (1975), reporting Hg concentrations between 0.16 and 0.48 μg/g. This study focused on evaluating the human health risk from the consumption of shrimp that are sold in local markets. Therefore, the objectives of this study were: i) to determine the concentration of THg and Se in the muscle of shrimp species from markets in the Pacific coastal zone of Mexico, ii) to estimate the methyl-mercury (MeHg) content, and iii) to provide Se:Hg molar ratio, the human health risk assessment and the permissible weekly shrimp consumption for Mexican populations along Pacific coast of Mexico.

For this baseline study, shrimp samples were collected from markets in the capital cities of the 11 coastal states of Mexico along the Pacific coast, between October 2021 and December 2022 (Fig. 1). At each sampling point (main city market), shrimp were obtained from three different stands (15 specimens/stand: a total of 45 specimens/market). Shrimp samples from different stands were not combined, were identified by their phenotypic characteristics, measured (total length (TL): from rostrum to telson), and were placed in plastic containers and transported to laboratory in freezers (4 °C). The shrimp samples collected were: white shrimp (*Litopenaeus vannamei*, TL: 12.15–18.03 cm) from Culiacán, Tepic, Guadalajara, Colima, Chilpancingo, Oaxaca and Tuxtla Gutiérrez; blue shrimp (*L. stylirostris*, TL: 15.75–17.86 cm) from Culiacán, Colima, Chilpancingo, Oaxaca and Tuxtla Gutierrez; brown shrimp (*Farfantepenaeus californiensis*, 13.77–18.11 cm) from Guadalajara, Colima, Morelia, Chilpancingo, Oaxaca and Tuxtla Gutierrez; and unidentified shrimp (penaeid shrimp) from La Paz, Mexicali and Hermosillo.

In the laboratory, the three composite samples by market (one for each stand, 15 specimens/composite sample) of edible muscle samples were obtained and placed in plastic containers. After that, tissues were lyophilized (−49 °C and 133 × 10^{-3} mbar) for 72 h; then the composite samples were ground in a Teflon mortar. The moisture percentage was determined by the difference of wet and dry weight of the samples. For each composite samples, three subsamples (nine subsamples/market) of 0.30 g were separated from each ground sample and digested overnight in 60 mL Savillex Teflon containers with 5 mL of concentrated nitric acid (HNO_3, trace metals grade) at room temperature in an extraction hood (Delgado-Alvarez et al., 2015). Digestion was carried out on a ceramic plate (Barnstead Thermoline) at 120 °C for 3 h. Subsequently, the digested samples were placed in plastic containers and diluted to 25 g with Milli-Q water. The Loring and Rantala (1992) method of cold vapor generation atomic absorption spectrophotometry (CV-AAS) was used to quantify THg by an Hg analyzer (Buck Scientific 410). Selenium was quantified by a Thermo element 2XR high-resolution ICP-mass spectrometer (HR-ICP-MS) (Soto-Jiménez et al., 2008).

For QA/QC, all materials used in sampling and metal analysis were washed according to Moody and Lindstrom (1977), which consisted of washing and rinsing with distilled water and acid washed with 2 M HCl and 2 M HNO_3; and finally, the material was rinsed with Milli-Q water. Certified reference materials (DORM-4 and DOLT-4 from National Research Council Canada; and NIST-1566b from National Institute of Standards and Technology) were used for THg and Se with satisfactory recovery percentages (93.4–112.15 %). Blanks were used to check contamination and all tissues were analyzed in triplicate. Detection limits were 0.01 μg/g for Hg and 0.007 μg/g for Se.

The human health risk was assessed through the hazard quotient (HQ) (Newman and Unger, 2002): HQ = E/RfD, where E is the level of exposure and RfD is the reference dose (Hg 0.1 μg/kg body weight/day) according to EPA (2010). The level of exposure (E) was calculated: E = C (I/W), where C is the Hg concentration (μg/g, wet weight) in the shrimp tissue, I is the apparent rate consumption of the product (in kg) per capita (1.93 kg/person/year for shrimp, equivalent to 5.29 g/day; CONAPESCA, 2020), and W is the average weight of an adult (70.7 kg) and a 10 years old child (28.8 kg) in Mexico (CANAIVE, 2012).

The Se:Hg molar ratio was calculated according to Burger and Gochfeld (2013). The health benefits value from selenium consumption (HBV_{Se}) was calculated as follows (Ralston et al., 2016):

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

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 a health risk could occur.

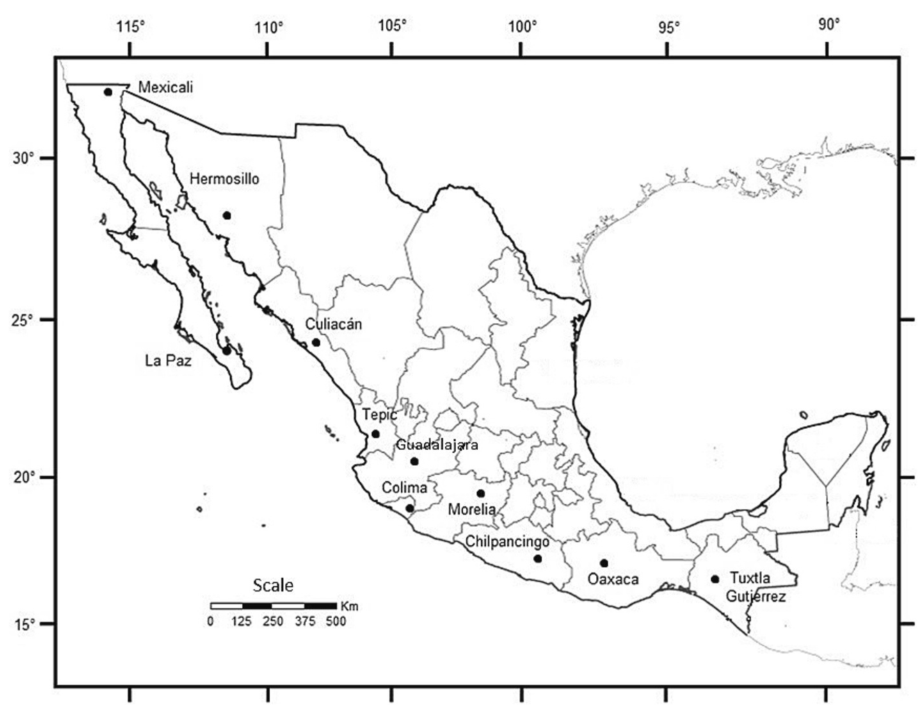

Fig. 1. Study area, City (State) in Mexico: Mexicali (Baja California), La Paz (Baja California Sur), Hermosillo (Sonora), Culiacán (Sinaloa), Tepic (Nayarit), Guadalajara (Jalisco), Colima (Colima), Morelia (Michoacán), Chilpancingo (Guerrero), Oaxaca (Oaxaca) and Tuxtla Gutiérrez (Chiapas).

Concentrations of THg in shrimp from the studied cities met the assumptions of normality (Kolmogorov-Smirnov test) and equality of variances (Bartlett test), and the parametric ANOVA was used. However, Se data were not normal (non-parametric); therefore, the comparison among cities were carried out by Kruskal-Wallis and the Dunn's methods. The THg and Se mean concentrations in the shrimp species were compared with a Kruskal-Wallis test and differences were identified by the Dunn's method. All analyzes were performed at a significance level of $p \leq 0.05$.

Table 1 shows the mean concentrations of THg and Se in the edible muscle of shrimp from markets in different states along Pacific coast of Mexico. The highest mean concentrations of THg were reported in La Paz (0.112 ± 0.043 μg/g ww) and Mexicali (0.102 ± 0.039 μg/g ww), while the lowest THg mean concentration was determined in the market of Tepic with 0.036 μg/g (ww). However, no significant differences ($p >$ 0.05) were observed among the 11 sampled points along Mexican Pacific coast.

The methyl-mercury (MeHg) concentrations were calculated using the THg/MeHg ratio (98.6 %) reported by Hoang et al. (2017). The highest MeHg value was recorded in La Paz with 0.110 μg/g (ww), while the lowest was obtained in Tepic with MeHg concentration of 0.036 μg/g (ww) (Table 1). The values obtained did not exceed the maximum limits allowed at the national level of 0.5 μg/g ww of MeHg according to NOM-242-SSA1-2009 (DOF, 2011).

For selenium, the mean concentrations ranged from 0.021 μg/g ww in Guadalajara, to 3.840 μg/g ww in Oaxaca. The statistical analysis showed a significant difference between the states located in the northwest of Mexico, compared to those in the south. Specifically, the cities of Mexicali (0.144 μg/g ww), Hermosillo (0.040 μg/g ww), Culiacán (0.037 μg/g ww) and Guadalajara (0.021 μg/g ww) showed significantly ($p < 0.05$) low concentrations than that of Oaxaca market.

Along the Mexican Pacific coast, the range of Se concentrations of the present study (0.021–3.84 μg/g ww) was higher than the interval reported by other authors in the same area. For THg, Frías-Espericueta et al. (2016) reported higher THg concentrations in the marine shrimp *L. stylirostris* and *F. californiensis* (0.810–1.610 μg/g, ww), while Frías-Espericueta et al. (2023) reported similar contents in the coastal shrimp *L. stylirostris*, *F. californiensis* and *L. vannamei* (0.052 –0.235 μg/g, ww), from NW Mexico.

Table 2 shows HQ values for Mexican adults and children, considering a body weight of 70.7 and 28.8 kg, respectively. The adult values were lower than those of children, ranging from 0.027 in Tepic, to 0.083 in La Paz. For children, the values ranged from 0.067 to 0.205 for the same cities. All HQ were < 1; indicating that there is no risk from shrimp consumption along the Pacific coast of Mexico, which coincided with the studies of Frías-Espericueta et al. (2016, 2023) in shrimp (marine and coastal shrimp) from NW Mexico.

Table 1
Concentration (μg/g, ww) of total mercury (THg) and selenium (Se) ± standard deviation and estimation of methylmercury (MeHg) in shrimp collected in Mexico's markets along Pacific coast.**

City	THg	MeHg	Se**
La Paz	0.112 ± 0.043a	0.110	0.700 ± 0.347ab
Mexicali	0.102 ± 0.039a	0.101	0.144 ± 0.046b
Hermosillo	0.086 ± 0.056a	0.085	0.040 ± 0.017b
Culiacán	0.079 ± 0.036a	0.078	0.037 ± 0.026b
Tepic	0.036 ± 0.014a	0.036	0.241 ± 0.084ab
Guadalajara	0.087 ± 0.039a	0.086	0.021 ± 0.002b
Colima	0.072 ± 0.045a	0.071	2.513 ± 0.280ab
Morelia	0.057 ± 0.006a	0.057	2.658 ± 0.215ab
Chilpancingo	0.075 ± 0.011a	0.073	2.513 ± 0.606ab
Oaxaca	0.091 ± 0.041a	0.089	3.840 ± 0.883a
Tuxtla Gutiérrez	0.076 ± 0.018a	0.075	1.746 ± 0.395ab

*Converted from Hoang et al. (2017) using a THg/MeHg ratio of 98.6 %.
**Non-parametric test. For given column, different letters indicate significant difference ($p < 0.05$).

Table 2
Hazard quotients (HQ) in adults and children, molar ratio (Se:Hg) and Se health benefit value (HBV_{Se}) in studied shrimp.

City	$THQ_{Hg\ Adults}$	$THQ_{Hg\ Children}$	Se:Hg	HBV_{Se}
La Paz	0.083	0.205	15.261	8.716
Mexicali	0.076	0.187	3.571	0.853
Hermosillo	0.064	0.158	1.685	−0.299
Culiacán	0.059	0.145	0.978	0.020
Tepic	0.027	0.067	21.545	3.040
Guadalajara	0.065	0.160	0.717	−0.547
Colima	0.054	0.132	121.068	31.826
Morelia	0.043	0.105	117.76	33.666
Chilpancingo	0.056	0.137	85.282	31.824
Oaxaca	0.068	0.167	127.735	48.626
Tuxtla Gutiérrez	0.057	0.140	58.933	22.101

In the context of Se:Hg molar ratios, Culiacán and Guadalajara markets showed a Se:Hg ratio < 1 (Table 2), which indicated that Se is not enough to counteract the occurrence of Hg. Regarding HBV_{Se}, Hermosillo and Guadalajara had negative values. These data could indicate that Se does not protect against Hg toxicity. However, the HQ values indicated that there is still no risk from the consumption of these organisms, due to its low Hg concentrations and the low national consumption. Unfortunately, there is not previous studies in Mexico regarding HBV_{Se} in shrimp.

A comparison of THg and Se concentrations among shrimp species was showed that *L. vannamei* presented significantly ($p < 0.05$) lower concentrations of THg (0.052 μg/g, ww), than those of *F. californiensis* (0.096 μg/g, ww) and penaeid shrimp (0.099 μg/g, ww) as shown in Table 3. The same trend was present in shrimp from the NW Mexico (Frías-Espericueta et al., 2023) where the THg concentrations showed the following order: *F. californiensis* > *L. stylirostris* > *L. vannamei*. A similar order was determined for Se content, although no significant differences ($p > 0.05$) were observed among shrimp species (Table 3). These THg and Se differences among shrimp species could be due to differences in feeding habits, biological activities and/or environmental Hg and Se levels (Francesconi and Lenanton, 1992).

In Mexico, the only previous study that showed mercury data in shrimp from markets was that of Reimer and Reimer (1975) carried out in Sonora and Sinaloa, with Hg values higher than those reported in the present work. Other studies that reported similar THg concentrations in shrimp from markets were from Italy (0.070 μg/g), Malaysia (0.064 μg/g) and China (0.061 μg/g) reported by Barone et al. (2015), Annual et al. (2018) and Yu et al. (2020), respectively; as shown in Table 4. However, the mean THg value from markets along Mexican Pacific coast, was higher than those reported in other studies in east China, Japan and Brazil (Table 4).

When comparing the mean THg concentration on wild shrimp obtained in this study with other national data (Table 4), the values tended to be similar. However, there was an exception with the THg concentration reported by Frías-Espericueta et al. (2023) for shrimp muscle with values 2.5 times higher than values of the present study.

The Joint FAO/WHO Expert Committee on Food Additives (JECFA, 2021) established a tolerable intake value of 1.6 μg MeHg/kg of body

Table 3
Mean total mercury (THg) and selenium (Se) content (μg/g, ww) in the muscle of *L. vannamei*, *L. stylirostris*, *F. californiensis* and penaeid shrimp from Mexican Pacific markets along Pacific coast.

Species	THg	Se
L. vannamei	0.052 ± 0.037b	1.265 ± 1.337ab
L. stylirostris	0.077 ± 0.045ab	1.564 ± 1.423ab
F. californiensis	0.096 ± 0.030a	2.306 ± 1.505a
Penaeid shrimp	0.099 ± 0.045a	0.335 ± 0.374b

*Kruskal-Wallis, Dunn's tests. Different letters indicate significant differences ($p < 0.05$) among species for the same element.

Table 4
Total mercury (THg) content (μg/g, ww) and hazard quotient (HQ) in shrimp from different zones.

Shrimp	Zone	THg	HQ	Reference
Markets				
F. californiensis	Mazatlán, Mexico	0.120	ND	Reimer and Reimer (1975)
L. stylirostris	Guaymas, Mexico	0.090	ND	Reimer and Reimer (1975)
P. kerathurus	South Italy	0.070	0.02–0.05	Barone et al. (2015)
L. vannamei	Japan	0.011	ND	Hoang et al. (2017)
P. merguiensis	W Peninsular, Malaysia	0.064	ND	Annual et al. (2018)
Shrimp	China	0.061	0.458	Yu et al. (2020)
Red shrimp	East China	0.030	ND	Zhang et al. (2020)
L. vannamei	Brazil	0.019	ND	Costa et al. (2021)
L. vannamei	Malaysia	0.030	0.00–0.19	Anuar et al. (2022)
Shrimp	Mexican Pacific coast	0.079	0.027–0.083	This study
Wild (Mexico)				
L. stylirostris	Altata lagoon, NW	0.075*	ND	Ruelas-Inzunza et al. (2004)
L. vannamei	Altata lagoon, NW	0.050*	ND	Ruelas-Inzunza et al. (2004)
L. stylirostris	NW marine zone	0.103*	ND	Frías-Espericueta et al. (2016)
F. californiensis	NW marine zone	0.070*	ND	Frías-Espericueta et al. (2016)
L. vannamei	Coastal lagoons NW	0.182*	0.550	Frías-Espericueta et al. (2023)
L. stylirostris	Coastal lagoons NW	0.195*	0.583	Frías-Espericueta et al. (2023)
F. californiensis	Coastal lagoons NW	0.203*	0.607	Frías-Espericueta et al. (2023)

* Transformed to wet weight, considering a humidity percentage of 75 %. ND: not determined.

weight/week. This value allows estimating the provisional tolerable weekly intake (PTWI), which is the maximum consumption (in grams) that do not represent a risk for adults and children. In this context, Table 5 shows that penaeid shrimp had the lower PTWI with 1159 g for adults and 472 g for children. However, it is still a safe maximum tolerable consumption, considering an estimated consumption of 37 g/person/week in Mexico (CONAPESCA, 2020).

As a general conclusion, the average concentrations of THg and MeHg did not exceed the maximum permissible limits established by Mexico. The hazard quotient (HQ) values for each sampling market along Mexican Pacific coast were <1, concluding that there is no human health risk due to shrimp consumption. However, some HBV_{Se} values were negative (Hermosillo and Guadalajara markets), indicating that there is no benefit or protection from Se in the specimens collected in that markets.

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CRediT authorship contribution statement

Alejandra Sánchez-Betancourt: Writing – review & editing, Methodology, Investigation, Conceptualization. **Carolina Guadalupe Delgado-Alvarez:** Writing – review & editing, Supervision, Investigation. **Pamela Spanopoulos-Zarco:** Writing – review & editing, Methodology, Investigation. **Jorge Ruelas-Inzunza:** Writing – review & editing, Methodology, Investigation. **Carmen Cristina Osuna-Martínez:** Writing – review & editing, Writing – original draft, Investigation. **Marisela Aguilar-Juárez:** Writing – review & editing, Investigation. **Martín Federico Soto-Jiménez:** Writing – review & editing, Supervision, Methodology, Investigation. **Mario Nieves-Soto:** Writing – review & editing, Investigation, Funding acquisition. **Alondra Guadalupe Sánchez-Rendón:** Methodology. **Martín Gabriel Frías-Espericueta:** Writing – review & editing, Writing – original draft, Project administration, Investigation, Funding acquisition, Conceptualization.

Table 5
Provisional tolerable weekly intake (PTWI) in grams of shrimp (from markets along Mexican Pacific coast) in adults (70.7 kg) and children (28.8 kg).

Shrimp species	PTWI	
	Adults	Children
L. vannamei	2206	899
L. stylirostris	1490	607
F. californiensis	1195	487
Penaeid shrimp	1159	472

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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