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Article

Mercury and Selenium Levels in Blue Shark (*Prionace glauca*) Along the California Current Ecosystem: Assessing Human Health Risks

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Abstract: Research on trophic transfer of trace elements in food chains, particularly toxic elements like mercury (Hg) and essential elements like selenium (Se), is crucial for understanding their impact on human health. In this work, we assessed the transfer of Hg and Se in the blue shark (*Prionace glauca*), a top predator with economic importance. Muscle samples from 23 sharks, as well as their main prey (squid, red shrimp, sardine, and mackerel), were analyzed for Hg and Se concentrations. The mercury levels of sharks were below the recommended legal limit for seafood consumption in Mexico ($1 \mu\text{g.g}^{-1}$ ww), while selenium levels were significantly lower than previously reported for the species. The biomagnification was evaluated in this species by calculating biomagnification factors (BMF) for mercury (Hg) and selenium (Se) based on predator-prey element concentrations. Hg showed a BMF of 2.8, indicating biomagnification, while Se had a BMF of 0.2, suggesting biodilution. Trophic transfer factor models supported these findings, showing a positive correlation of Hg concentration with trophic level and a negative correlation with Se. Consumption of blue shark muscle poses no risk based on hazard quotient analysis, but caution is advised due to Hg biomagnification.

Keywords: elasmobranch fisheries; biomagnification; biodilution; Mexican Pacific; trophic transfer models

Key Contribution: This study is the initial assessment of biomagnification and biodilution of Hg and Se in blue sharks throughout the Mexican portion of the California Current Ecosystem.

1. Introduction

Trophic transfer of essential and potentially toxic trace elements in marine food webs is an important environmental research area [1]. In particular, heavy metals such as mercury (Hg) are of great concern, since they may be transferred from the abiotic aquatic environment (water, sediments) to living organisms with accumulation in diverse components of food chains and with a potentially toxic effect. While Hg is naturally emitted mainly from volcanoes, geothermal sources, and soils, it is continually recycled and re-emitted to the atmosphere and deposited on the sea surface [2]. However, over the last century, the total Hg concentration in the marine environment has increased drastically due to anthropogenic sources [3]. Methylmercury (MeHg) is the most toxic form of this element due to its capacity for absorption through cell membranes, producing several physiological changes like

oxidative stress and neurotoxicity among others [4]. In that sense, a full comprehension of global sources, speciation, and transport of Hg is necessary to understand the final contribution to MeHg production in aquatic systems, and therefore to its accumulation and transfer among wildlife [5].

In aquatic systems, pH, dissolved organic matter, and oxygen have a remarkable influence on the Hg cycle [6]. Mercury methylation rates depend to some extent, on the availability of electron acceptors (O, N, S, Fe) because they influence the metabolism of sulfate-reducing bacteria [7]. Thus, acidic waters and reducing conditions, associated with low dissolved oxygen (O_2), favor Hg methylation. Some processes connected with global climate change, such as the expansion of the minimum oxygen zones (MOZ) in the tropics, can modify and enhance the presence and abundance of Hg methylation microbiota [8], ultimately increasing MeHg availability. Additionally, it is known that long-lived top predatory fishes such as sharks, through processes like bioaccumulation and biomagnification, tend to have high concentrations of MeHg in their tissues, particularly in muscle (edible part), which may have serious implications for wildlife and human health [9].

In contrast, selenium (Se) is an essential element for all organisms that are distributed globally in organic-rich sedimentary rocks. Most of its forms can be quickly transformed and incorporated into food webs [10]. Indeed, organic Se is the most bio-available chemical form, so the primary route of exposure to Se in marine consumers is through the diet rather than the water [11]. However, this element is also supplied to aquatic systems as a by-product of several human activities such as coal-fired energy plants, agriculture, refining of crude oil, and coal mining, leading to elevated levels of Se. These elevated levels have resulted in the degradation of several ecosystems and have been linked to reproductive impairment in important fish species [12]. Selenium is also known to prevent Hg toxicity in the body, through an interaction mechanism that occurs in the organism when both elements are present in high concentrations [13]. Mercury binds to Se with high affinity, so there is enough evidence suggesting that during the antagonistic interaction, MeHg sequesters the available Se in the body, preventing it from performing its essential physiological roles. Therefore, Hg poisoning can lead to symptoms resembling a Se deficit [14].

Mercury magnification in the food web is a form of bioaccumulation, often measured using the Biomagnification Factor (BMF) to compare contaminant levels in predators and prey [15]. But recently a more comprehensive approach has been proposed where the biomagnification potential of an element from a lower to a higher trophic level could be determined by a Trophic Transfer Factor (TTF), obtained from the slope of logarithmically concentrations of chemicals in organisms versus the trophic levels of the organisms in the food chain [16].

Blue sharks are one of the most abundant apex predators worldwide and therefore one of the main species of fish caught by longline fisheries, which certainly occurs along the California Current Large Marine Ecosystem (CCLME) [17]. This species can accumulate high levels of toxic elements through their diet, potentially reaching unacceptable levels for consumption [18]. Blue sharks are not commonly traded in the U.S. due to the low quality of their meat [19], but they are captured in Mexico for human consumption locally and for exportation [20]. So, the current conservation status of this species has raised concern due to the global demand for its meat, fins, and liver oil [21]. In Mexico, blue shark catches make up a significant portion of fisheries landings (about 80%), with most of the catch (90%) being consumed domestically due to its availability and low cost. [22]. This study aimed to quantify the dietary contribution to the accumulation of mercury (Hg) and selenium (Se) in the muscle of blue sharks, considering the high potential of biomagnification of Hg and the possible biodilution of Se due to its antagonistic behavior, with the final purpose to assess the potential human health risks associated with consuming this shark meat.

2. Materials and Methods

2.1. Collection of Specimens

Twenty-three blue shark specimens were collected from oceanographic campaigns carried out by the Mexican Institute for Research in Sustainable Fisheries and Aquaculture (IMIPAS) between 2019 and 2023 in the north Mexican Pacific (Figure 1). The sharks were captured using hook lines during the closed season from May to July. Specimens that did not survive the tagging process were retained for further study. Each shark's weight, length, and sex were recorded, and muscle tissue samples (20 g) were collected and stored at -4°C. Additionally, samples of the blue shark's main prey items in the study area were collected [23–25], including the red crab (*Pleuroncodes planipes*), the squid (*Gonatus* spp.), the anchovy (*Engraulis mordax*) and the mackerel (*Scomber japonicus*) (Figure 1). Prey items were collected with a trawl net.

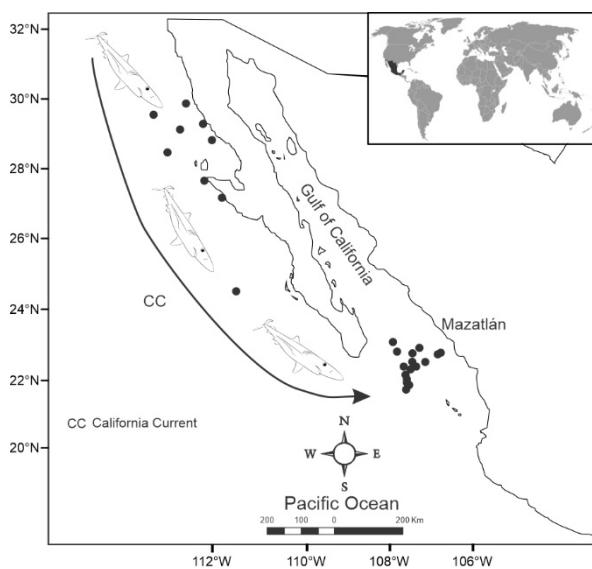


Figure 1. Sampling stations where blue shark and their prey were collected in the southern part of the California Current Ecosystem.

2.2. Sampling Procedure

Blue shark muscle and complete prey organisms were freeze-dried (140×10^{-3} mBar; -49°C) for 72 h on Labconco equipment. Dry tissues were manually ground in an agate mortar. Homogenized powdered samples were digested with concentrated nitric acid (69%) (Trace Metal Grade) in stoppered vials for 3h at 120°C [26]. Concentrations of Se were measured by graphite furnace-atomic absorption spectrophotometry (GF-AAS) with Zeeman correction background (AAnalyst 800, Perkin-Elmer) equipment. In addition, concentrations of Hg were measured by cold vapor-atomic absorption spectrophotometry (CV-AAS) in Buck Scientific equipment. Quality control of elemental analyses included blanks, duplicates, ultra-pure water (milli-Q, $18.2\text{ M}\Omega\text{ cm}$), trace metal grade acids, and reference materials. Reference materials used were obtained from the National Research Council of Canada, dogfish muscle (DORM-3) for shark and fish samples, and lobster hepatopancreas (TORT-2) for squids and red crabs. The recovery percentage was $105 \pm 7.4\%$ (Se) and $101 \pm 0.1\%$ (Hg) in DORM-3 and $103 \pm 0.06\%$ (Se) and $100 \pm 0.32\%$ (Hg) in TORT-2. The limits of detection (two times the standard deviation of a blank) were $2.1\text{ }\mu\text{g/L}$ for Se and $0.11\text{ }\mu\text{g/L}$ for Hg. Conversions of concentration units from dry weight to wet weight were calculated considering the humidity percentage in muscle (for shark and fish tissue 75%) and for invertebrates (squids and crabs 50%) respectively. Concentration units of Se and Hg are given as $\mu\text{g.g}^{-1}$ wet weight.

2.3. Data Analysis

BMF was calculated using equation 1 [27]:

$$\text{BMF} = [\text{element}]_{\text{predator}} / [\text{element}]_{\text{prey}}. \quad (1)$$

BMF calculations were made based on the assumption that the concentrations of elements (Hg and Se) have reached a steady state in the sampled tissues. $\text{BMF} > 1$ indicates that biomagnification of the element is occurring [28].

The TTF to assess the biomagnification or biodilution of an element through the sample food chain was analyzed by equations (2) and (3) [29]:

$$\log_{10}[\text{element concentration}] = a + b * \text{TL} \quad (2)$$

$$\text{TMF} = 10^b \quad (3)$$

Where a is the intercept of the regression between $\log_{10}[\text{element concentration}]$ and TL (trophic level), depending on the element background concentrations [30], b is the slope of the regression line [31] representing the biomagnification or biodilution capacity of an element [32].

Finally, the antilog of the slope b which is the relationship between \log_{10} transformed concentrations ($\mu\text{g.g}^{-1} \text{ww}$) and TL, is used to calculate the TTF. Predator and prey TL was taken from bibliographic references [33]. Biomagnification causes a $\text{TTF} > 1$. So, TTF above 1 implies a disequilibrium between organisms and the media (water) that increases with the TL. Slope b was weighted by linear regression for both elements. The correlation coefficient (R^2) was assessed using the Pearson method (statistically significant at $p < 0.05$). Both simple linear models were displayed with R software (R Core Team, 2024).

We calculated the hazard quotient (HQ) of Hg concentrations in the muscular tissues of the blue shark. Values of HQ were calculated using equation 4 [34]:

$$\text{HQ} = E / RfD \quad (4)$$

Where E is the exposure level or intake of total Hg, RfD is the reference dose for total Hg (0.5 $\mu\text{g/kg}$ body weight/day) [35], and the Exposure level is calculated from equation 5:

$$E = C \times I / W \quad (5)$$

Where C is the concentration of total Hg in the edible part of the fish in wet weight, I is the intake rate of shark meat expressed in grams per day per capita, determined as 17.38 $\text{g} \cdot \text{day}^{-1}$ for the local population [36]; W is the weight of an average adult in Mexico (70 Kg).

3. Results

3.1. Mercury and Selenium Assessment

Firstly, when comparing mercury (Hg) levels in the blue shark prey, we found that they were consistently higher than previously reported values in the study area for three species (*P. planipes*, *S. japonicus*, and *E. mordax*). Previous studies in the area [22] reported Hg concentration values below 0.05 $\mu\text{g.g}^{-1} \text{ww}$, while our results showed values above 0.2 $\mu\text{g.g}^{-1} \text{ww}$ in all reported prey (Table 1). The Hg average concentration in the muscle of the shark *P. glauca* was below the recommended limit of 1 $\mu\text{g.g}^{-1} \text{ww}$ set by national and international standards [36,37] (Table 1). In contrast, selenium (Se) levels were lower than those previously reported for some prey [22], where authors reported values of 0.83 $\mu\text{g.g}^{-1} \text{ww}$ for *S. japonicus* and 0.90 $\mu\text{g.g}^{-1} \text{ww}$ for *P. planipes*, while the mean Se values in this study were below 0.35 $\mu\text{g.g}^{-1} \text{ww}$ (Table 1).

Table 1. Mean concentrations of Hg and Se ($\mu\text{g}\cdot\text{g}^{-1}$ ww) for the blue shark and their prey items with the individual BMF for each element and [Se]/[Hg] molar ratio.

Organism	N	TL	Hg	BMF_Hg	Se	BMF_Se	Se/Hg
<i>P. planipes</i>	10	2.4	0.22	2.82	0.35	0.23	4.02
<i>Gonatus</i> sp.	10	2.6	0.20	3.07	0.27	0.29	3.49
<i>S. japonicus</i>	5	3.9	0.23	2.70	0.32	0.25	2.21
<i>E. mordax</i>	5	3.9	0.24	2.63	0.21	0.38	4.46
<i>P. glauca</i>	22	4.5	0.63		0.08		0.41

Nevertheless, molar ratios above 1 in all of the preys suggested a molar excess of Se, so in consequence, this element could be available to protect the organism against Hg toxicity.

3.2. Trophic Transfer Models

The trophic transfer factor estimated through models was significant, indicating that mercury (Hg) is biomagnified along the blue shark diet (Figure 2a) while selenium (Se) is diluted (Figure 2b) through the food chain.

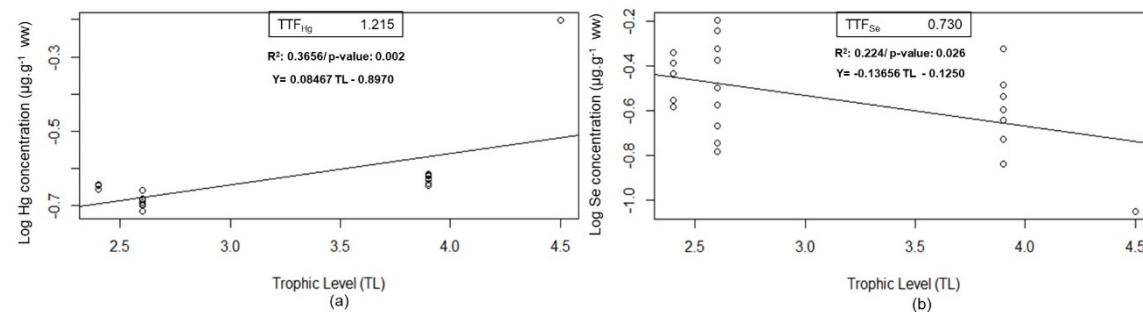


Figure 2. Variation of mercury (Hg) (a) and selenium (Se) (b) logarithmic concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ ww) with the trophic level (TL) of predator (blue shark) and its preys (red crab, squid, mackerel, sardine); Trophic transfer factors (TTF) for each element based on models results.

3.2. Risk Assessment

The HQ estimated for each shark category were all below 1, indicating no risk of consumption (Table 2). However, sensitive population sectors such as pregnant or breastfeeding women and children should always be mindful of the amount of this species consumption.

Table 2. HQ values in the muscle of blue sharks according to Hg concentrations and ingestion rate.

Category	N	HQ
Males	16	0.34
Females	6	0.24
Adults	12	0.41
Juveniles	10	0.10
All	22	0.16

4. Discussion

4.1. Mercury and Selenium Trophic Transfer

Because of its widespread presence, toxicity, and ability to accumulate in organisms, Hg has been frequently used to study biomagnification in marine food webs [29]. Sharks, with their

reproductive strategy (K), high trophic level, and economic significance, are commonly used as models to study the biomagnification process of this contaminant [37]. The dietary route plays a main role in determining toxic element burdens in marine organisms. Seafood is considered the major source of Hg intake in the human diet, but it also provides essential minerals like Se which serve as enzymatic cofactors and offer other health benefits [38].

Bioaccumulation of Hg in the muscle of blue sharks captured in the southern part of the California Current Ecosystem, which occurs in the Mexican North Pacific has been confirmed and reported before, where adults showed a bigger concentration of Hg in muscle [39]. Under this scene, we consider it relevant to investigate if biomagnification of this toxic metal was also taking place in this species. Food serves as a vehicle for both toxic and beneficial elements, so apex predators, including humans, are exposed to high levels of these elements, potentially leading to organic dysfunctions [41]. While Se is essential within certain limits, excessive amounts can be harmful [42]. Most research on this topic agrees that Hg and Se should be assessed together due to their antagonistic relationship [43]. Selenium proteins are involved in mercury neutralization once they get into the body to prevent its toxicity, so when an organism has high levels of Hg, it is likely to have low levels of Se available [44]. Therefore, it is crucial to monitor the concentration of both elements in marine products intended for human consumption.

Accordingly, our results show that biomagnification of Hg and Se biodilution occurs at the same time in this top predator. This phenomenon could be attributed to the Hg detoxification process where most of the Se available in the organism would be involved in the demethylation of MeHg to give place to inorganic Hg-Se compounds [40]. Finally, this compound (Hg-Se) reacts with selenoproteins altering vital functions mainly involved in oxidative stress [41]. It has been repeatedly suggested that Hg concentration increases along the food chain to explain the levels well above reference values in organisms living in the open sea [42]. This is mainly because long-lived, slow-growing, and highly migratory oceanic fishes such as sharks tend to accumulate high concentrations of Hg, especially in the muscle, which can often exceed recommended limits for human consumption [43].

However, other authors who aimed the same biomagnification hypothesis in the North-eastern Atlantic Ocean, found that BMF remained always <1 suggesting that biomagnification of Hg does not occur in this species [44]. In contrast, in the Mexican Pacific previous studies reported that prey contains less Hg than predators but didn't estimate the BMF, while also remarking that the main source of this toxic metal throughout the diet of the shark could be the pelagic red crab (*P. planipes*), due to the large amount of it that the predator need to consume to compensate the lack of energy that this small prey can offer [23]. So it is relevant to point out that Hg concentration found for this species after 15 years is almost 4 times higher. It is worth mentioning that this species is also commercial, caught, and used for preparing animal feed for aquaculture which finally will end up being consumed by humans.

4.2. Health risk Assessment

The shark fishery in the Mexican Pacific is a relevant food resource not only locally but globally since Mexico is one of the main producers and exporters of this shark species [45,46]. IMIPAS, through various monitoring programs (such as the shark observer programs) and specifically the tagging of blue sharks on board oceanographic cruises, has revealed that catches of this species for human consumption have been increasing due to the growing demand for its products due to its low cost [47]. Nevertheless, the results of this program after 15 years show that the blue shark population in the Mexican Northwest Pacific stays stable and is not under overfishing pressure [48]. Therefore, it is important to keep in mind the potential risks to human health that high levels of Hg accumulated in the edible parts of this shark can cause. One way to address this issue is the non-carcinogenic risk assessment method using the HQ established by the United States Environmental Protection Agency [49]. This approach assumes that there is a level of exposure to the toxic metal (the reference dose,

RD) below which even the most sensitive sectors of the population are unlikely to experience adverse health effects [50].

Based on the results of our hazard quotient estimation, we could state that there is no risk for consumers of blue shark meat since all values were less than 1. However, taking into account that bioaccumulation and biomagnification of Hg occur in this species, it would be most prudent to recommend moderate consumption. In previous works with the same organisms sampled, we stipulated a daily consumption dose of this species that can be consumed without presenting risks of Hg poisoning, so under this calculation, an intake between 11.9 and 10.9 g per day can be recommended for an adult man or woman in Mexico [39]. These results are similar to those proposed for the Mediterranean where the maximum consumption rate of blue shark is 10 g per day [51]. In this sense, considering that shark meat is a great source of essential elements, but also the main Hg route of entry to humans, certain precautionary measures must be taken especially when the specimens consumed are adults and the consumers belong to the more sensitive population sector (pregnant and breastfeeding woman and child).

5. Conclusions

This study assessed the levels of mercury (Hg) and selenium (Se) in blue sharks in the CCLME region. While the sample size was limited, the data suggests a potential increase in Hg and a decrease in Se with higher trophic levels. Additionally, Hg and Se concentrations were found in prey species not previously studied in the area, which are also consumed by humans. The Hazard Quotient analysis recommends a weekly consumption limit of 70g of edible muscle of this shark species to avoid Hg poisoning risk for consumers.

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Institutional Review Board Statement: “The study was conducted under the Ethics Code of the Institute of Marine Sciences and Limnology, and all the samples were legally obtained with the appropriate fishing permits issued by the National Commission for Fisheries and Aquaculture”

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors upon request.

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Conflicts of Interest: “The authors declare no conflicts of interest.”

Abbreviations

The following abbreviations are used in this manuscript:

BMF	Biomagnification Factor
TTF	Trophic Transfer Factor
CCLME	California Current Large Marine Ecosystem
TL	Trophic Level
IMIPAS	Mexican Institute for Research in Sustainable Fisheries and Aquaculture

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