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Mercury and Selenium Bioaccumulation in the Smooth Hammerhead Shark, *Sphyrna zygaena* Linnaeus, from the Mexican Pacific Ocean

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Abstract We analyzed total mercury and selenium bioaccumulation in muscle tissue and cartilage fibers (fins) from smooth hammerhead shark, *Sphyrna zygaena*, caught off Baja California Sur, Mexico. In muscle tissue, the mercury concentration ranged from 0.005 to 1.93 $\mu g\ g^{-1}$ ww (wet weight), which falls within the safety limits for food set by international agencies (Hg > 1.0 $\mu g\ g^{-1}$ ww). Only one specimen showed a mercury value that exceeded this limit. In fins, the mercury bioaccumulation was lower (<0.05). Selenium in muscle ranged from 0.11 to 1.63 $\mu g\ g^{-1}$ ww, while in fins it ranged from 0.13 to 0.56 $\mu g\ g^{-1}$ ww.

Keywords Bioaccumulation · Mercury · Selenium · *Sphyrna zygaena*

Heavy metals are substances with a chemical equilibrium regarding biodegradation processes. They do not disappear from the environment, because they are transferred to others places and they can change of state or produce other substances (Svobodová et al. 1993). One of these heavy metals is mercury, which is a highly toxic pollutant that occurs in the natural environment as a result of human or volcanic activities. More than 90% of the total mercury in certain fish tissues is in the methylmercury form (CH_3Hg), an organic complex produced by bacteria from inorganic mercury. Therefore, the measurement of total mercury provides an approximation of methylmercury and has been recommended as the standard for regulatory monitoring (Adams and McMichael 1999).

The highest levels of methylmercury are found in the predatory fish at the top of the food chain due to bioaccumulation. This methylmercury bioaccumulation characteristic tends to magnify in the food chain in long lived top predators (Eisler 1981), such as the smooth hammerhead shark *Sphyrna zygaena*, it which is an important species in commercial catches of regional fisheries and the meat is marketed fresh or dry and salted. Therefore, the accumulation of mercury in fish is a concern because of potential human health effects from fish consumption, as well as potential effects on fish-eating wildlife. However, one natural fish component that may protect against Hg toxicity is selenium (Se), due to the interaction between the two elements (Cardellicchio et al. 2002). According to Kaneko and Ralston (2007), the interactions between mercury and selenium are essentials factors in evaluating risks associated with dietary exposure to mercury. Even so, little is known on Hg:Se relationship in sharks (Storelli and Marcotrigiano 2002; Kaneko and Ralston 2007). International agencies such as the Food and Drug Administration and the World Health Organization have established fish consumption advisories of 1.0 $\mu g\ g^{-1}$ Hg wet weight for many countries, including Mexico, where the Mexican Official Norm follows this limit. Therefore, the aim of this study is to determine the mercury and selenium accumulation in muscle (edible) and cartilage (fin) tissues of 37 specimens of *S. zygaena* from the western coast of Baja California Sur, Mexico. We also investigated the relationships between shark sex and size and metal concentration in the

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tissues; and the mercury level of the main prey of *S. zygaena*.

Materials and Methods

Thirty-seven sharks were collected from San Lázaro (24°45′N; 112°8′W), and Las Barrancas (26°04′N; 112°16′W), off the western coast of Baja California Sur (Fig. 1). We obtained samples monthly from May 2006 to November 2007 from sharks caught by fishermen using gill-nets. For each specimen, total length (TL) was measured in the field to the nearest 1 cm and sex was recorded. A sample of 5.0 g of dorsal anterior muscle tissue was taken from each shark using a scalpel previously sterilized. We also collected the caudal fin, and the skin was removed to analyze the cartilage's fibers, which are used in shark fin soup. Prior to analysis, the specimens were dissected to extract the stomach contents. We chose the main prey of *S. zygaena* (Ochoa-Díaz 2009) that presented a minimum degree of digestion in order to obtain muscle tissue. Sediment or other inappropriate material that might contaminate the samples was removed with deionized water. Samples were wrapped in aluminum foil, labeled and stored in a freezer at −20°C in the Laboratory of Fish Ecology at Centro Interdisciplinario de Ciencias Marinas (CICIMAR-IPN) until mercury analysis was carried out in the Laboratory of Toxicology of Veterinary Medicine and Zootechny Faculty at Universidad Nacional Autónoma de México (FMVZ-UNAM).

To determine the mercury levels in *S. zygaena*, muscle samples of *S. zygaena* and their prey were dried and their water content was determined by weight loss after drying. The samples were dried in electric desiccators at 45°C during 24 h. The dried muscle was homogenized by grinding using an agate mortar and pestle. Afterwards, samples were stored individually in plastics bags previously labeled.

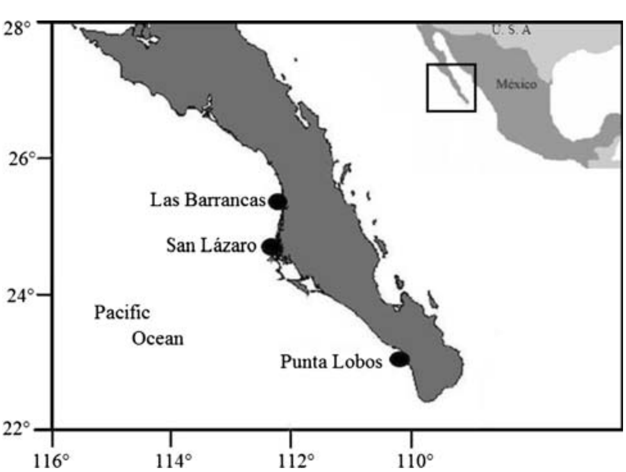

Fig. 1 Study area

From each sample of dried muscle, one subsample of 0.5 g (dry weight) was digested by 2 mL distilled water, 3 mL nitric acid and 1 mL hydrogen peroxide in a microwave closed system (in vials of the electromagnetic digester in a closed system) (CEM MDS-2000) during 1 h approximately, in order to ensure the complete destruction of organic compounds containing the metal. Total Hg and Se were determined using an Atomic Absorption Spectrophotometer by hydride generation (Perkin Elmer AAnalyst 100), with a detection limit of 0.05 μg. Readings were taken at a wavelength of 253.7 nm for mercury and 256 nm for selenium. For mercury, potassium permanganate is added to eliminate possible interference. The absorbance (peak height) is measured as a function of mercury and selenium concentration by means of a regression analysis. Mercury and selenium concentrations were expressed as micrograms per gram (μg g^{-1}) on the dry (dw) and wet weight (ww) basis of the tissue. The wet weight basis was obtained using as reference an overall average percentage of moisture in the tissue. The accuracy of analysis procedures was verified by validating the certificated reference material (CRM). This reference was provided by the International Atomic Energy Agency, Monaco (IAEA-407). The samples were analyzed with blanks and replicates during the readings. To test the normality of the mercury bioaccumulation data, we used a Kolmogorov–Smirnov test. However, the mercury levels were not normally distributed ($p < 0.05$), so we used logarithmic transformations to normalize the data and reduce heteroscedasticity. Linear regressions were used to examine relationships between shark total length and total mercury level. The level of significance for statistical tests was 0.05 (Zar 1984). Non-detectable values were set at half the detection limit for the metal for statistical analyses.

Results and Discussion

The results of quality controls obtained from the analysis of validation are given in Table 1, and show a good agreement with certified data. Total mercury and selenium concentrations in edible muscle and fins of *S. zygaena* are shown in Table 2. Mercury levels in the muscle of this shark ranged from 0.005 to 1.93 μg g^{-1} ww (0.025–7.62 μg g^{-1} dw) with an average of 0.16 μg g^{-1} ww and median of 0.10 μg g^{-1} ww (Av. = 0.73 μg g^{-1} dw; median = 0.45 μg g^{-1} dw) (Table 2). Lowest mercury levels were recorded in the fins (cartilages' fibers) ([Hg] μg g^{-1} ww < 0.009; n = 15). The smooth hammerhead shark, *S. zygaena*, contains levels of mercury than are within the safety limit set by international agencies.

Although one specimen showed mercury value that exceeded this limit (Hg > 1.0 μg g^{-1} ww), this specimen was a female shark with the largest size reported in this study (184 cm LT). For females, the average mercury content was 0.20 μg g^{-1} ww (0.86 μg g^{-1} dw), while males had an average of 0.12 μg g^{-1} ww (0.56 μg g^{-1} dw). There are often high variations in mercury concentrations between individuals within a local population, due to several factors that can affect the mercury bioaccumulation in fishes, particularly in predators such as sharks, which are at the top of the food chain, are long lived, and tend to have higher Hg concentrations than other marine organisms. These factors are fish age, size, mercury concentration in the ecosystem, food contamination, position of the fish in the food chain, chemical, biological and physical processes in the aquatic environment and seasonal variations. Our results showed that mercury concentrations were low in comparison with the study of García-Hernández et al. (2007) carried out in the Gulf of California, Mexico for the smooth hammerhead (*S. zygaena*). They found the highest concentration of total mercury level in mature organisms (272 cm; av. 8.25 mg/kg ww). In contrast, Mársico et al. (2007) found mercury concentration in *S. zygaena* of 0.433 μg g^{-1} dry weight (average) in the southern Brazilian coast, which is lower that our data. It is important to mention that although the peninsula of Baja California Sur is considered undeveloped and pristine, it has important mineral deposits (Shumilin et al. 2000), which contribute to high regional variability in heavy metal concentrations in coastal waters off Baja California that have been attributed to both natural (e.g. upwelling and water column mixing) and anthropogenic (e.g. phosphorite mining and urbanization) causes (Shumilin et al. 2001). However, hammerhead sharks are migratory organisms, and they can obtain the mercury in others waters.

The relationship between total length (TL) and mercury bioaccumulation was not significant ($R^2 = 0.009$, n = 37, $p = 0.01$), therefore mercury does not increase with the size of sharks (Fig. 2). Animal size is, in fact, recognized to be important in determining the rate of physiological processes that influence uptake, distribution and elimination of metals. In our study, the lack of correlation between total length and mercury levels cannot be evidence of effective detoxification mechanisms since we would need a large size range to say that the accumulation in muscle tissue of *S. zygaena* increased with size. However, Núñez-Nogueira et al. (1998) mentioned that the corporal detoxification mechanism is inversely proportional to size. One element that protects against mercury toxicity is selenium, which plays an important role in enzymatic activities. The relation between selenium and mercury must be 1:1 to have a protective effect (Cabañero et al. 2007). However, in our data this proportion was not equitable, so that the selenium bioaccumulation in edible muscle was higher than mercury and ranged from 0.53 to 7.06 μg g^{-1} dw (0.11–1.63 μg g^{-1} ww), while in fins it ranged from 0.66 to 1.72 μg g^{-1} dw (0.13–0.56 μg g^{-1} ww). Muscle selenium bioaccumulation did not correlate with mercury concentration (Fig. 3).

Table 2 Mercury and selenium bioaccumulation in muscle and fin of the smooth hammerhead shark, *Sphyrna zygaena*, caught off the western coast of Baja California Sur, Mexico

Element	Tissue	Range	Average	Median
Hg	Muscle	0.005–1.93	0.73	0.10
	Fin	0.005–0.009	0.007	0.008
Se	Muscle	0.11–1–63	0.34	0.27
	Fin	0.13–0.56	0.35	0.34

The main preys of the smooth hammerhead shark for the western coast of Baja California Sur are cephalopods such as *Dosidicus gigas*, *Onychoteuthis banksii*, *Ancistrocheirus lesueurii* and *Stenoteuthis oualaniensis* (Ochoa-Díaz 2009). These preys were analyzed in this study to determine their mercury level and to determine which prey provides the principal quantity of mercury to the predator and show the possible biomagnification phenomenon. The cephalopod, *A. lesueurii* was the prey with the highest mercury level with an average of 0.86 μg g^{-1} dw (0.13 μg g^{-1} ww; n = 2), followed by the jumbo squid, *D. gigas* (av. 0.34 μg g^{-1} dw; n = 13), *S. oualaniensis* (0.21 μg g^{-1} dw; 0.04 μg g^{-1} ww; n = 1) and *O. banksii* (0.11 μg g^{-1} dw; 0.02 μg g^{-1} ww n = 1). Therefore, *A. lesueurii* is the prey with the greatest transference of mercury. Gray (2002) mentioned that biomagnification is not a universal rule in marine ecosystems. In particular some contaminants, such as metals, are fairly easily eliminated from organisms and do not accumulate. Only organic mercury is not as quickly depurated and is more easily biomagnified in higher trophic level

Table 1 Results of the analysis of standard reference materials (IAEA-407) obtained during this study

Element	n	Found (μ g^{-1})	Certified value av. (range)	% Measured value
Hg	10	0.206	0.22 (0.22–0.23)	93.6
Se	3	2.05	2.85 (2.7–2.96)	72.4

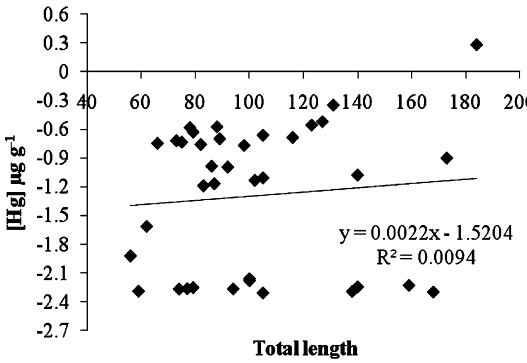

Fig. 2 Relationship between total mercury expressed in μg g^{-1} wet weight and total length (cm) for smooth hammerhead shark

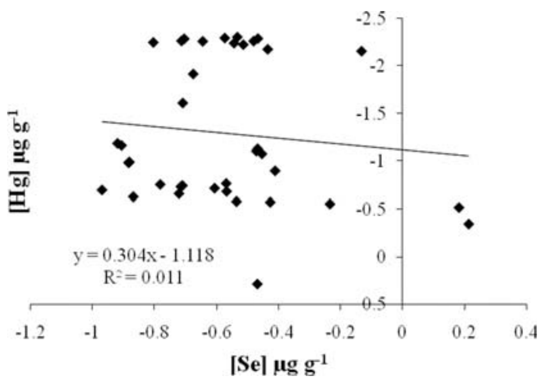

Fig. 3 Relationship between total mercury and selenium expressed in μg g^{-1} wet weight

animals. This process could be seen when substances are transferred from food to an organism, resulting in higher concentrations compared with the source (Gray 2002). According to Bustamante et al. (2006), it has been demonstrated that cephalopods have special capabilities to accumulate heavy metals at various levels in their tissues, although dissimilar information on Hg concentrations in cephalopods and on their variations have been reported. In our data, the mercury levels of sharks were higher than the mercury levels of their prey. Therefore, this prey (cephalopods) could be the major route of mercury bioaccumulation in sharks. Mainly *A. lesueurii*, was the prey with the highest level of mercury, although its concentrations present no risk for human consumption. However, it is difficult to determine a trend with such a small sample size of prey.

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