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Bioaccumulation and Biomagnification of Total Mercury in Four Exploited Shark Species in the Baja California Peninsula, Mexico

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Abstract The present study determined the average mercury bioaccumulation in the muscle tissue of four shark species (*Carcharhinus falciformis*, *Prionace glauca*, *Sphyrna zygaena* and *Isurus oxyrinchus*) captured in the Baja California Peninsula. We also evaluated biomagnification of some prey consumed by sharks. All sharks' species had mercury levels over the limit specified by the Mexican government for human consumption. Blue shark (*P. glauca*) presented highest mercury values (1.96 ± 1.48 µg/g Hg d.w.) and it was the unique specie that showed a negative correlation with mercury content ($Rs = -0.035, p = 0.91$). *Scomber japonicus* was the prey with high content of mercury (0.57 ± 0.02 µg/g).

Keywords Mercury · Bioaccumulation · Biomagnification · Shark · Pacific Ocean · Mexico

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Industrialization and artisanal mining of precious metals have contributed to the increment of toxic contaminants in the environment, affecting mainly coastal areas. One such contaminant is mercury, which is an element not essential to life (Núñez-Nogueira et al. 1998); it is, however, naturally present in the environment due to geological processes like erosion, degasification of the earth's crust and volcanic emissions. Mercury can be found under two essential forms in aquatic systems: inorganic (Hg^{+1}, Hg^{+2}) and organic ($HgCH_3$). The latter form is the result of biomethylation reactions in biological systems; where the methyl-B12 co-enzime transforms inorganic mercury salts into methylmercury and dimethylmercury. The high toxicity of ionic mercury and of methylmercury is due to their great affinity for amino and sulphydril protein groups, forming metallic complexes that hinder the ability of enzymes to control metabolic reactions (Campos 1987).

Aquatic organisms can absorb mercury through biotic and abiotic processes, concentrating these substances in their tissues and organs (bioaccumulation) (Rand et al. 1995). This bioaccumulation occurs mainly in fishes, especially in large long-lived predators like sharks, whose muscular tissues can present high mercury levels through the union of metal to the proteins (Gomes et al. 2004).

So, mercury is transferred through the trophic web, and their concentration increases at each level (biomagnification); they are present in marine mammals and humans, causing negative health effects. It is important to evaluate mercury levels in aquatic animals in order to alert the public to the effects of consuming contaminated animals, and to determine the physiological differences among species relating to different elimination mechanisms and metal accumulation. The present study determined: (1) mercury bioaccumulation in smooth hammerhead shark (*Sphyrna zygaena*), blue shark (*Prionace glauca*), mako shark (*Isurus oxyrinchus*) and silky shark (*Carcharhinus falciformis*), and (2) biomagnification of this metal through their main prey (jumbo squid, pelagic red crab, chub mackerel and lantern fish) in seven locations along the Baja California peninsula (Mexico). Four sites were on the west coast of the peninsula: Las Barrancas (26°04′N; 112°16′W), San Lázaro (24°45′N; 112°8′W), Punta Belcher (24°34′N; 112°05′W) and Punta Lobos (23°25′N; 110°15′W); and three on the Gulf of California: Punta Arenas (24°03′N; 109°49′W), El Sauzoso (24°18′26″N; 110°38′17″W), and El Portugués (24°47′38″N; 110° 39′39″W).

Materials and Methods

Specimens were collected between 2001 and 2005 using traditional fishing methods (gill nets and hooked lines). Each individual was identified to species; we determined the sex and measured total length (T_L). Approximately 10 g of muscle tissue were collected from the dorsal area. Samples were covered in aluminum foil and stored frozen at 4°C. Analyses were carried out at the Toxicology Laboratory of from the Universidad Nacional Autonoma de Mexico (UNAM).

We additionally collected prey specimens that are part of the diet of the four shark species studied in the Baja California area. Jumbo squid *Dosidicus gigas* were collected at night with hooks from small watercraft in the Santa Rosalía area. Mackerel *Scomber japonicus* were captured using seine nets deployed from boats in Bahia Magdalena and pelagic red crab *P. planipes* were collected from tuna stomach contents. All samples were kept frozen at 4°C. We also obtained data of mercury concentrations in lantern fish *Symbolophorus evermanni* (the squid's most important prey) from the Inter-American Tropical Tuna Commission.

Mercury concentration analysis was carried out at the UNAM laboratory. 5.0 g of shark and prey tissue were dehydrated in an oven at 60°C for 24 h. Samples were then digested with nitric acid and hydrogen peroxide in an electromagnetic digester MARS5, CERM Corporation. Finally, samples were gauged to 25 mL with deionized water, and were read using the hydride generation technique in an atomic absorption spectrophotometer Perkin Elmer Analyst 100 in order to determine mercury concentrations (µg/g). After, we converted mercury concentrations in ng/g to µg/g. Data was reported on dried weight (d.w.).

Shark muscle data were grouped by species, sex and length. Normality and independence were evaluated using Kolgomorov-Smirnov's test and homogeneity of variances using Burr-Foster's test (Q-test). To estimate the effect of species and sex relative to mercury concentration we used the Kruskal–Wallis test to determine in which species analyzed, the mercury concentrations differed.

For the effect of length on mercury concentration in each species we applied Spearman correlations (R_s), due to our data were out of normal distribution.

According to Gray's definition (2005) the increase in concentration between trophic levels could reflect the biomagnification phenomenon, therefore we measured the mercury level in lower trophic levels (main preys of sharks) to established the prey with major probability to biomagnified.

Results and Discussion

Over the 5 years of this study we collected 91 muscle samples belonging to four shark species. Of these, 68 muscle samples were analyzed for sex and length; unfortunately, data were not record for 23 sharks (Table 1), but it were analyzed only to obtain the percent of samples of each species that had levels of mercury higher than those established by Mexican law (NOM-027-SSA1 1993), since we did not have information about sex and length for those samples.

All of *C. falciformis*, 90% of *P. glauca*, 33% of *I. oxyrinchus* and 29% of *S. zygaena* irrespective of size or sex, had levels of mercury higher than those estimated as fit to be consumed by humans according to Mexican law (1.0 µg/g; NOM-027-SSA1 1993). On average, *C. falciformis*, *I. oxyrinchus* and *P. glauca*, have muscle mercury concentrations above 1.0 µg/g, while smooth hammerhead shark, *S. zygaena* however, presents mercury values below

Table 1 Number total and subtotals of organisms analyzed, including the average of total length (T_L) and sex according to shark species (N = sample size)

Shark species	N Total	N Subtotal	N Males	N Females	T_L (mean ± standard deviation)
P. glauca	21	12	10	2	206.2 ± 52.8
C. falciformis	15	15	8	7	196.6 ± 20.2
I. oxyrinchus	24	20	11	9	127.1 ± 37.9
S. zygaena	31	21	9	12	114 ± 19.2
Total	91	68[a]	38	30	

[a] Data (sex and T_L) were not record for 23 specimens

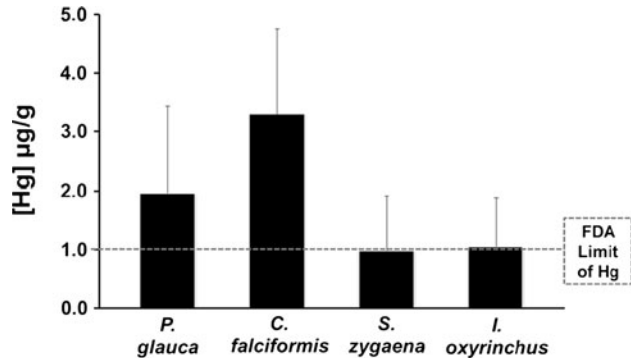

Fig. 1 Average mercury bioaccumulation in muscle of shark species caught off Baja California Peninsula, Mexico. *Dashed line* represents the limit of mercury in meal to consumption established by Food and drug administration (FDA)

1 µg/g, although close to one (Fig. 1; Table 2). This mercury build up in sharks is linked to the fact that they are long-lived species, showing slow growth, low fecundity, and a high trophic level. These characteristics contribute to a substantial accumulation of mercury in their tissues (Lyle 1981).

The significant differences in mercury concentrations found among shark species are due to the differential availability of prey with dissimilar mercury contents, and to the mercury contained in sediments, water and suspended organic matter with which the species interact. Bio-availability of this trace metal also depends on the chemical and physical properties of the environment, specific biochemical processes, the physiology of each species and reproductive aspects. *C. falciformis*, *S. zygaena* and *P. glauca* are viviparous placental species, presenting an umbilical cord. This implies that since their embrionary development sharks start accumulating mercury transferred from the mother, and this contributes to the detected metal concentrations in their muscular tissue from birth (Adams et al. 1999).

Carcharhinus falciformis presented the highest mercury concentration in this study. This can be explained by the fact that it is an epipelagic predator commonly found in coastal areas, where there is a higher productivity of prey species than in the open ocean (Cabrera-Chávez et al. 2010), compared to other species with more oceanic (*P. glauca*) or benthic habits (*S. zygaena*). Coastal preys that are consumed in higher amounts by *C. falciformis* are more exposed to potential anthropogenic and natural contaminations in the area.

Most *I. oxyrinchus* individuals were collected in the western coast of Baja California Sur, which are areas where juvenile mako sharks feed, being found at shallow depths and close to shore (Velasco-Tarelo 2005). These sharks' diet is therefore based on prey found in coastal areas, which implies that they are more exposed to contaminants. Mako shark mercury concentrations in this study presented mercury intervals below those reported by Watling et al. (1981) off the coasts of Australia (2.36–22.32 µg/g Hg dry weight). It is possible that the individuals analyzed in that study were adults and had higher levels of mercury in their tissues or organs, unlike what was observed in the present study, where we only analyzed juveniles.

Sphyrna zygaena presented an average mercury concentration (0.98 ± 0.92 µg/g Hg), ten times lower than that obtained by Storelli et al. (2003) in Italy, who found concentrations of mercury in muscle of 48.6 ± 4.6 µg/g Hg. This result indicates that there could be higher mercury concentrations in Mediterranean waters and that mercury residency time of the analyzed specimens in the Gulf of California and the western Pacific coast is so short that mercury is not yet present at higher trophic levels. Metal accumulation is attributed to the feeding habits of this shark since it is an efficient predator on benthonic organisms such as fish, crustaceans and cephalopods.

Blue shark (*P. glauca*) presented highest mercury values (1.96 ± 1.48 µg/g Hg). Its concentrations were above the range reported by Branco et al. (2004) for the Atlantic (0.60–4.04 µg/g Hg). This result could be due to 83% of analyzed individuals being juveniles; this could imply that they had a shorter exposure time to mercury than adult individuals, which move to deeper waters away from shore. Adults have pelagic feeding habits (epipelagic-mesopelagic prey); their prey lives in oceanic waters less exposed to contamination. Therefore mercury ingestion by blue sharks is not constant, resulting in a decrease in concentration as time goes by.

All juveniles and adults of *C. falciformis* had concentrations over 1.0 µg/g, the highest percentage compared to

Table 2 Total mercury concentrations in muscle sharks caught in the Baja California peninsula, Mexico

Shark species	N Total	Total mercury (µg/g) dry weight		
		Mean ± standard deviation	Minimum	Maximum
P. glauca	21	1.96 ± 1.48	0.76	6.52
C. falciformis	15	3.40 ± 1.42	1.06	5.84
I. oxyrinchus	24	1.05 ± 0.82	0.44	4.21
S. zygaena	31	0.98 ± 0.92	0.24	2.8
Total	91			

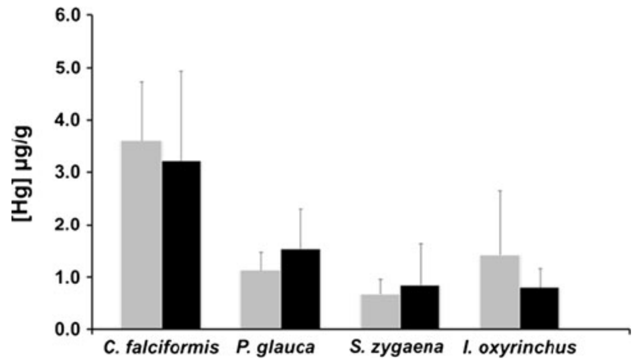

Fig. 2 Mean concentration of mercury measured in muscle of shark species caught off Baja California peninsula, Mexico

the other species analyzed. 75% of *P. glauca* juveniles and 87.5% of adults were above 1.0 µg/g; 35% of *I. oxyrinchus* juveniles and 19% of *S. zygaena* also had levels above 1 µg/g.

We found significant differences among the shark species analyzed for length and mercury concentration ($p < 0.05$), but we did not find significant differences for sex ($p > 0.05$) relative to these two variables (Fig. 2).

A direct relationship between mercury concentration and size were found, except for *P. glauca* (Fig. 3). In some occasions, sharks group according to size and sex when feeding. This occurs in *C. falciformis*, which segregate by sex and are nearly always found close to each other (Carrier et al. 2004). They present similar trophic habits, feeding mainly on pelagic red crab (Cabrera-Chávez et al. 2010); however *I. oxyrinchus* juveniles do not present this segregation and both sexes feed on the fish *Prionotus albirostris* (Velasco-Tarelo 2005). This behavior is reflected in our results; we did not find differences between sexes with respect to mercury concentration for the four shark species.

Linear regression showed certain tendency for mercury concentration to augment at larger sizes, showing that younger sharks have been exposed for less time to the metal than the adults. *C. falciformis* presented the second best quadratic relationship, followed by *S. zygaena*. Ontogenic trophic changes has been observed in sharks, due to larger individuals have more efficient predation mechanisms and are adapted to capturing larger and faster prey (Cabrera-Chávez et al. 2010). This agrees with different studies carried out on elasmobranchs, which show that food remains in the digestive tract for long time periods (18 days) in comparison with most teleosts (Wetherbee et al. 1990). The evidence suggests that the elimination rate in elasmobranchs is very slow and for this reason these species bioaccumulate greater mercury concentrations.

Blue sharks did not show a clear linear regression relationship (this was negative). This is probably due to the fact that the individuals captured were adults. Another hypothesis that can explain this is the possibility that this species presents more efficient mercury elimination mechanisms due to a higher synthesis of metallothioneine, a protein charged with detoxication (Núñez-Nogueira et al. 1998). Blue sharks might store metal in intracellular granules over long time periods in order to eliminate them

Fig. 3 Correlation analysis of mercury concentration (µg/g) relative to length in four shark species off the Baja California Peninsula, Mexico. **a** *I. oxyrinchus,* **b** *S. zygaena,* **c** *P. glauca* and **d** *C. falciformis*

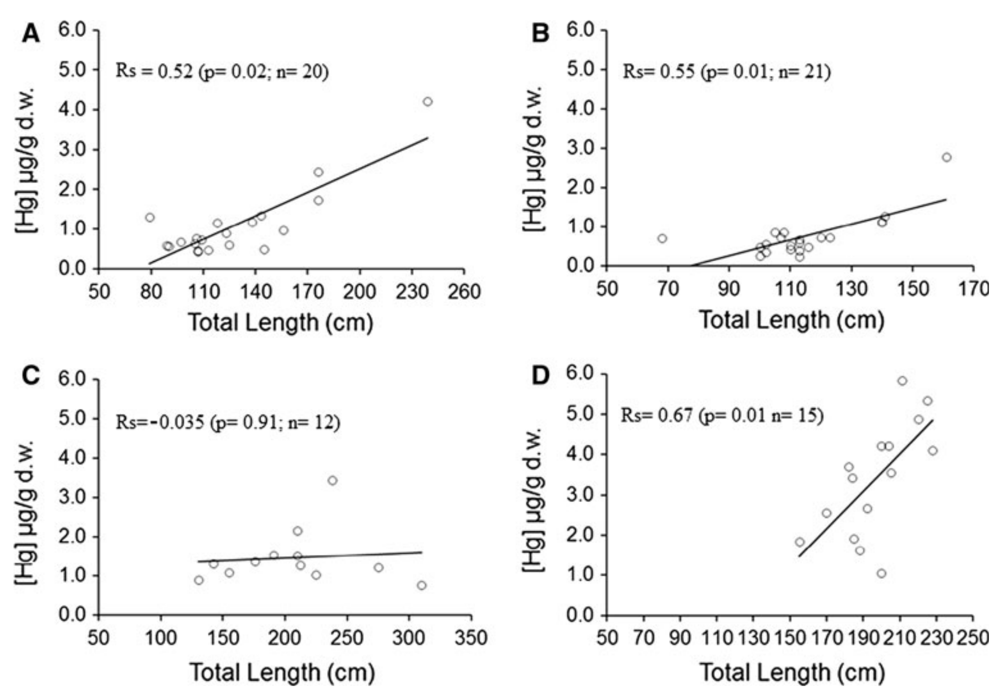

Table 3 Average mercury concentration (μg/g) of shark prey

Preys	Average ± SD
D. gigas (giant squid)	0.12 ± 0.05
P. planipes (red crab)	0.13 ± 0.01
S. japonicus (chub mackerel)	0.57 ± 0.02
S. evermanni (lantern fish)	0.34 ± 0.13

by defecation (Fitgerald 2004), or they might metabolize and excrete mercury more effectively if selenium is present (Cuvin-Aralar and Furness 1991). However, it would be helpful to carry out studies to determine whether the low mercury concentrations seen in *P. glauca* are due to such processes.

We observed that biomagnification of mercury could occurred through the food web for the four shark species studied. Mercury concentration in prey was variable and lower than that found in sharks. The mackerel, *S. japonicus* presented the highest average mercury concentration (0.57 ± 0.02 μg/g Hg), followed by lantern fish *S. evermanni* (0.34 ± 0.13 μg/g Hg). The lowest mercury concentrations were found in pelagic red crab *P. planipes* (0.13 ± 0.01 μg/g) and giant squid *D. gigas* (0.12 ± 0.05 μg/g Hg) (Table 3).

Most prey (mackerel, pelagic red crab and squid) that have been reported to be part of sharks' diet (Cabrera-Chávez et al. 2010) bioaccumulated metal and transferred it to their predators. However, it has to be considered that sharks can change their diet according to their ontogenetic stage, and this contributes to mercury accumulation in their tissues with time (Wetherbee et al. 1990).

Gray (2002) defines biomagnification as the increase in concentration between trophic level. According to this definition, we observed that all prey types can bioaccumulate mercury, but in smaller amount than shark. *C. falciformis* presented the highest biomagnification in its trophic chain, since this species tends to bioaccumulate mercury as it is a coastal species.

The transfer is not reflected in the mercury obtained for cephalopods. This can be explained by their rapid metabolism, fast growth rates and short life span, which is manifested in high mortality (Martínez-Aguilar et al. 2004). These characteristics allow them to have short exposure times and an effective metal elimination, avoiding high organic mercury accumulations in their tissues and organs. According to our study, the prey that transferred the highest mercury concentration to sharks was *S. japonicus*, one epipelagic specie that feed on zooplanckton, but one important factor to be considered is the biomass would play a very important role in bioaccumulation and biomagnification of this metal.

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