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Baseline

# Mercury in muscle and liver of ten ray species from Northwest Mexico

J. Ruelas-Inzunza [a,*], O. Escobar-Sánchez [a], J. Patrón-Gómez [a], X.G. Moreno-Sánchez [b], A. Murillo-Olmeda [a], M. Spanopoulos-Hernández [a], D. Corro-Espinosa [c]

[a] Technological Institute of Mazatlán, Environmental Section, P.O. Box 757, Calle Corsario 1, No. 203, Col. Urías, C.P. 82070 Mazatlán, Sinaloa, Mexico
[b] Instituto Politécnico Nacional-CICIMAR, Av. Instituto Politécnico Nacional S/N, C.P. 23096 La Paz, BCS, Mexico
[c] Centro Regional de Investigaciones Pesqueras de Mazatlán, INAPESCA, Calzada Sábalo-Cerritos S/N, 82010, P.O. Box. 1177, Mazatlán, Sinaloa, Mexico

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ABSTRACT

We determined total mercury (Hg) distribution in muscle and liver of ten ray species and assessed health risk considering Hg levels in muscle and average consumption of rays in Mexico. Rays were collected from five sites in NW Mexico between March and November 2012. Hg concentrations ranged from 4.465 $\mu g\ g^{-1}$ in muscle of the longtail stingray *Dasyatis longa* to 0.036 $\mu g\ g^{-1}$ in liver of the diamond stingray *Dasyatis dipterura*. Considering all the individuals, Hg in muscle (1.612 ± 1.322 $\mu g\ g^{-1}$) was significantly ($p < 0.05$) higher than in liver (0.745 ± 0.616 $\mu g\ g^{-1}$). Regarding local health risk assessment, none of the ray species may cause adverse effects on consumers.



Mercury is potentially toxic to humans, the main source of which is seafood. The conversion of inorganic Hg to the methylated form in the aquatic ecosystem is critical in terms of its presence in food (Carrington and Bolger, 2002). It is known that methyl mercury (MeHg) concentration increases towards more elevated trophic levels (Dietz et al., 2000). Considering that 90% or more of the total Hg in fish is in the form of MeHg (Hall et al., 1997), ichthyofauna at the top of trophic chains might be in risk as well as human consumers. Moreover, rays are consumed in Mexico and it is necessary to know if Hg is above maximum permissible limits (1.0 $\mu g\ g^{-1}$ wet weight) in the Mexican legislation (Ruelas-Inzunza et al., 2012).

Studies related to the occurrence of Hg in top predators indicate that pelagic sharks (Escobar-Sánchez et al., 2011; Maz-Courrau et al., 2012) accumulate elevated concentrations of Hg. To our knowledge, in NW Mexico only two studies (García-Hernández et al., 2007; Gutiérrez-Mejía et al., 2009) related to the presence of Hg in rays have been published. The aims of the study were: (a) to determine Hg distribution in muscle and liver of collected specimens and (b) to assess potential health risks considering Hg levels in the edible portion of rays (muscle) and average consumption of rays in Mexico.

Rays were captured in five sites of NW Mexico (Fig. 1): Puerto Chale (site 1) and El Portugués (site 2) in Baja California Sur; El Choyudo (site 3) Sonora; Dautillos (site 4) Sinaloa, and Playa del Rey (site 5) Nayarit. Specimens were caught by local fishermen using gill nets between March and November 2012. Rays were identified according to illustrated taxonomic keys (Fischer et al., 1995). Laboratory materials used for handling, transportation and dissection of biota were acid washed according to Moody and Lindstrom (1977). Size (disc width) and total weight of specimens were determined in the laboratory. In the case of *Rhinobatos productus* and *Narcine entemedor* from El Portugués (site 2), total length of specimens was determined instead of the disc width. Muscle and liver were extracted by dissecting specimens using stainless steel scalpels. Samples were freeze-dried in a Labconco Freeze-dry System (FreeZone 6) at $76 \times 10^{-3}$ mBar and −53 °C (72 h). Dried samples were ground in an agate mortar with pestle (Fischer Scientific). Powdered samples (0.25 g) were digested with concentrated nitric acid (J.T. Baker; trace metal grade) in capped Teflon vials (Savillex) at 120 °C for 3 h (MESL, 1997). Hg analyses were made by cold vapor atomic absorption spectrophotometry (CV-AAS) in a Buck Scientific mercury analyzer (UNEP, 1993). Quality control of the analytical process was assessed by using certified reference materials (DORM-3, fish protein; DOLT-4, dogfish liver). Blanks and reference materials were run with every batch of samples. The limit of detection of Hg was estimated in 0.012 $\mu g\ g^{-1}$ dry weight. Mean recovery was 109%; coefficient of variation of reference materials were 0.7% and 0.1% for DORM-3 and DOLT-4, respectively. Results are reported in $\mu g\ g^{-1}$ on a dry weight basis. Human health risk was estimated by the hazard quotient (HQ) according to Newman and Unger (2002): $HQ = E/RfD$ ($E$ is the intake of Hg; RfD is the reference dose for Hg = 0.5 $\mu g\ kg^{-1}$ of body weight of a person day$^{-1}$). Hg intake was estimated as $E = C * I/W$ ($C$ is the concentration of Hg in muscle of rays, $I$ is the ingestion rate of rays in Mexico = 0.82 g day$^{-1}$, and $W$ is the weight of an average adult = 70 kg). It is worth mentioning that the ingestion rate of the edible portion of rays in Mexico is non-existing;

* Corresponding author. Tel.: +52 669 9838400; fax: +52 669 9847209.
*E-mail address:* ruelas@ola.icmyl.unam.mx (J. Ruelas-Inzunza).

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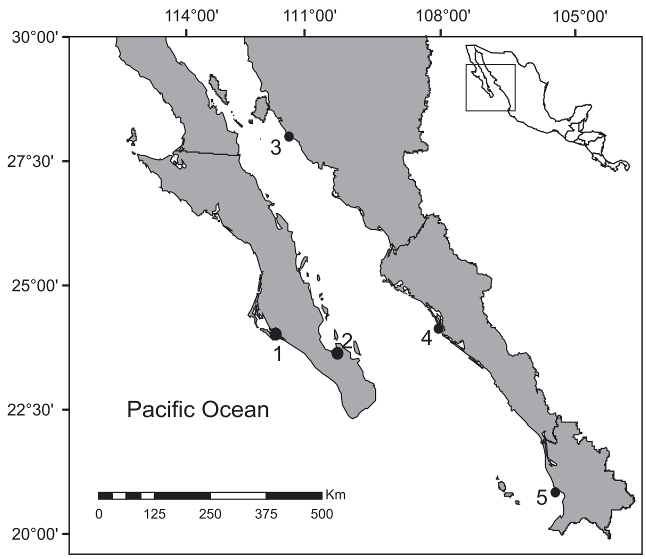


**Fig. 1.** Sites of collection of rays in Northwest Mexico.

estimations were made according to published data for average consumption of sharks in Mexico (CONAPESCA, 2005). Hg concentrations on a dry weight basis ($Hg_{dw}$) were converted to fresh weight basis ($Hg_{fw}$) according to Magalhães et al. (2007): $Hg_{fw} = Hg_{dw} * (100 - \% \text{ humidity})/100$, using 70% of moisture in muscle tissue of rays. Differences in metal concentrations between muscle and liver were defined by a Student *t* test using GraphPad Prism 4.0 (Graph Pad Software, San Diego, CA).

Collected specimens corresponded to ten ray species and six families (Table 1). Considering the diversity and abundance of collected rays, the family Dasyatidae was better represented than the rest of the families in the study area. Hg concentrations ranged from 4.465 $\mu g\ g^{-1}$ in muscle of the longtail stingray *Dasyatis longa* to 0.036 $\mu g\ g^{-1}$ in liver of the diamond stingray *Dasyatis dipterura* (Table 1). Considering averaged concentrations of Hg in muscle ($1.612 \pm 1.322\ \mu g\ g^{-1}$) and liver ($0.745 \pm 0.616\ \mu g\ g^{-1}$) of all the species, values were significantly ($p < 0.05$) different. In the case of the intraspecific comparison between muscle and liver, *D. dipterura* showed significantly ($p < 0.05$) higher levels of Hg in muscle. There is not a clear trend of Hg distribution between muscle and liver of elasmobranchs; in the sharks (*Rhizoprionodon terranovae* and *Carcharhinus limbatus*) and rays (*Rhinoptera steindachneri*) it was found that muscle accumulated more Hg than liver (Núñez-Nogueira et al., 1998; Gutiérrez-Mejía et al., 2009). In benthic fish there was an inverse behavior; i.e. Hg levels in liver were higher than in muscle (Bustamante et al., 2003). It is known that soon after metal exposure, distribution to tissues may be influenced by the administration route; i.e. elevated concentration in the skin could imply a recent exposure to contaminated sediments or high concentrations in the gastrointestinal mucosa following dietary exposure (Kleinow et al., 2008). Higher levels of Hg in muscle of elasmobranchs may indicate that the element was mainly taken through the diet, distributed in the body and cumulatively stored in muscle; on the other hand, lower Hg concentrations in liver might be associated to metabolic and elimination processes (Pethybridge et al., 2010). In the liver there is the reaction of Hg with selenium (Se) to form mercuric selenide, this is considered as an effective mechanism for counteracting the damaging effect of Hg in elasmobranchs (Storelli and Marcotrigiano, 2002).

In comparison to rays from Florida (0.73 $\mu g\ g^{-1}$, averaged from six species; Adams et al., 2003) and Greenland (0.2–0.4 $\mu g\ g^{-1}$, range for one ray species; Joiris et al., 1997); Hg values in muscle of several ray species (1.21 $\mu g\ g^{-1}$, averaged from fifteen species; García-Hernández et al., 2007; Gutiérrez-Mejía et al., 2009; our study) from the Gulf of California were higher. In a compilation of studies with Hg concentrations in elasmobranchs, concentrations were usually below 2.0 $\mu g\ g^{-1}$ (on a dry weight basis) in specimens collected in the North Atlantic Ocean (Eisler, 2010). In our study, Hg concentrations in muscle ($1.612 \pm 1.322\ \mu g\ g^{-1}$) were comparable; in liver, concentrations ($0.745 \pm 0.616\ \mu g\ g^{-1}$) were an order of magnitude lower. With respect to Hg levels in the edible portion of analyzed species and in comparison to maximum permissible limits in the Mexican legislation (1.0 $\mu g\ g^{-1}$ wet weight; Ruelas-Inzunza et al., 2012), *D. longa* and *Urolophus* spp. had Hg levels above the referred value. In comparison to international legislations (Canada and Brazil) that have set lower thresholds (0.5 $\mu g\ g^{-1}$ wet weight), *D. dipterura*, *D. longa*, *U. halleri* and *Urolophus* spp. showed Hg concentrations above the legal limit. It is worth mentioning that *Urolophus* spp. and *U. halleri* are not con-

**Table 1**
Biometric information, collection sites, Hg concentrations ($\mu g\ g^{-1}$ dry weight) and HQ of collected rays from Northwest Mexico.

| Species | Common name | *N* | Disc width (cm) | Site (code) | *L* | *M* | HQ |
|---|---|---|---|---|---|---|---|
| Family Dasyatidae | | | | | | | |
| *Dasyatis dipterura* | Diamond stingray | 24 | 46.3 ± 8.4 | El Choyudo (3) | 0.036 ± 0.03 | 0.946 ± 0.63 | 0.006 |
| *Dasyatis dipterura* | Diamond stingray | 6 | 33.9 ± 5.1 | Playa del Rey (5) | 0.83 ± 0.9 | 2.84 ± 2.4 | 0.02 |
| *Dasyatis longa* | Longtail stingray | 1 | 52.7 | Playa del Rey (5) | 0.071 | 4.465 | 0.031 |
| *Urolophus halleri* | Haller's round ray | 10 | 36.9 ± 7.1 | El Portugués (2) | 0.723 ± 0.63 | 1.37 ± 1.6 | 0.009 |
| *Urolophus halleri* | Haller's round ray | 1 | 22.0 | Playa del Rey (5) | 1.90 | 2.33 | 0.016 |
| *Urolophus spp.* | Round stingray | 1 | 22.8 | Playa del Rey (5) | 1.90 | 3.713 | 0.026 |
| Family Urotrygonidae | | | | | | | |
| *Urotrygon chilensis* | Chilean round ray | 5 | 26.8 ± 1.4 | Puerto Chale (1) | 0.70 ± 1.1 | 0.52 ± 0.83 | 0.003 |
| Family Rhinobatidae | | | | | | | |
| *Rhinobatos productus* | Shovelnose guitarfish | 2 | 65.0[a] ± 15.5 | El Portugués (2) | 0.73 ± 0.1 | 0.89 ± 1.1 | 0.006 |
| *Zapteryx exasperata* | Banded guitarfish | 1 | 34.5 | Puerto Chale (1) | 0.423 | 0.898 | 0.006 |
| Family Narcinidae | | | | | | | |
| *Narcine entemedor* | Giant electric ray | 1 | 28.0[a] | El Portugués (2) | 1.205 | 0.101 | 0.0007 |
| *Narcine entemedor* | Giant electric ray | 1 | 29.0 | Puerto Chale (1) | 0.387 | 1.053 | 0.007 |
| Family Rajidae | | | | | | | |
| *Raja velezi* | Round stingray | 1 | 83.0 | El Portugués (2) | 0.049 | 1.127 | 0.008 |
| Family Gymnuridae | | | | | | | |
| *Gymnura marmorata* | California butterfly ray | 1 | 50.0 | Dautillos (4) | 0.734 | 0.706 | 0.005 |

*N* – number of specimens; *L* – liver; *M* – muscle; HQ –hazard quotient.
[a] Total length.

sumed in the region. Hazard quotients (HQ) in collected rays from NW Mexico were very low even in those cases where Hg concentrations exceeded Mexican legal limits (1.0 $\mu g\ g^{-1}$ wet weight). Since HQ are calculated based on Hg levels in the edible portion as well as the rate of consumption, the daily consumption per capita of rays in Mexico (estimated as 0.82 g) is very low and it influences HQ calculation exerting a decreasing effect. As a result of the above considerations, none of the estimated HQ poses a health risk for consumers. Though HQ were low, more information about the actual rate of consumption of rays among fishermen and their families, and the analysis of methyl Hg in the edible portion of elasmobranchs is necessary.

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