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Mercury concentrations in three ray species from the Pacific coast of Baja California Sur, Mexico: Variations by tissue type, sex and length

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ABSTRACT

Total mercury concentrations ([THg]) were determined in muscle and liver of the bat ray (*Myliobatis californica*), shovelnose guitarfish (*Pseudobatos productus*) and banded guitarfish (*Zapteryx exasperata*). Generalized linear models (GLM) were used to determine the effects of size and sex in [THg] and showed that both are determinants of [THg] in these species. The [THg] in both tissues significantly increased with length especially in sexually mature organisms with a steeper slope for mature male than mature female. This may relate to elasmobranchs sexual dimorphism driven variation in growth rates. Median muscle [THg] was significantly greater than liver in each ray species but there were some individuals with higher liver [THg] than muscle. There were individuals with muscle [THg] higher than the advisory thresholds of 0.2 and 0.5 mg kg^{-1} ww (2.4 and 11% of the bat ray; 2.1 and 10% of the shovelnose guitarfish; 12.6 and 45% of the banded guitarfish, respectively).

1. Introduction

Sharks and rays are important fishery resources for human consumption worldwide (Domi et al., 2005; Ramírez-Amaro et al., 2013) and their meat is rich in nutrients such as protein, omega-3 polyunsaturated fatty acids, vitamins and minerals, (Olmedo et al., 2013; Gribble et al., 2015; Matos et al., 2015). In contrast to their health benefits, some species accumulate high concentrations of mercury (Hg), due their longevity, size, slow growth, high trophic status and low fecundity (Kim et al., 2016).

Monomethyl mercury ($MeHg^+$) is a well-known neurotoxicant that has been subject to intense research, due to its potential adverse effects and ability to bioaccumulate and biomagnify in marine food webs (Horvat et al., 2014; Hosseini et al., 2013). Toxicity depends on the chemical form and bioavailability, $MeHg^+$ comprises up to 90% of total mercury (THg) found in muscle of most fish (Adams and McMichael, 1999; Escobar-Sánchez et al., 2010; Hosseini et al., 2013) and between 70% and 100% in rays species (Storelli et al., 2002; Horvat et al., 2014) that is readily absorbed from the diet and crosses the blood brain barrier and placenta (Brookens et al., 2007; Correa et al., 2013). As a result, human populations with traditionally high dietary fish intake are exposed to $MeHg^+$ (Olmedo et al., 2013; Matos et al., 2015).

Most studies assessing THg concentrations ([THg]) in elasmobranchs focused mainly on sharks and to a lesser extent batoids (Escobar-Sánchez et al., 2013). Particularly, on the Pacific coast of Baja California Sur (PCBCS), México, elevated [THg] have been reported for some commercially important shark species (e.g. blue shark, *Prionace glauca*; Escobar-Sánchez et al., 2011; Maz-Courrau et al., 2011; Barrera-García et al., 2012). However, there is a lack of information regarding several species of shark, especially batoid species that constitute part of the local diets.

The most important species in the artisanal elasmobranchs gillnet fishery of the PCBCS are the bat ray (*Myliobatis californica*), shovelnose guitarfish (*Pseudobatos productus*) and banded guitarfish (*Zapteryx exasperata*) (Ramírez-Amaro et al., 2013). While these species are used for human consumption, especially in coastal areas little is known about the potential human health impacts of the consumption of their meat.

We examined [THg] in muscle and liver tissue of the bat ray, shovelnose guitarfish and banded guitarfish, collected in the PCBCS. Our study analyzes the interactions of tissue type, body size and sex on [THg] for each of the three ray species and compares concentrations between species for liver and muscle. We evaluated [THg] in muscle

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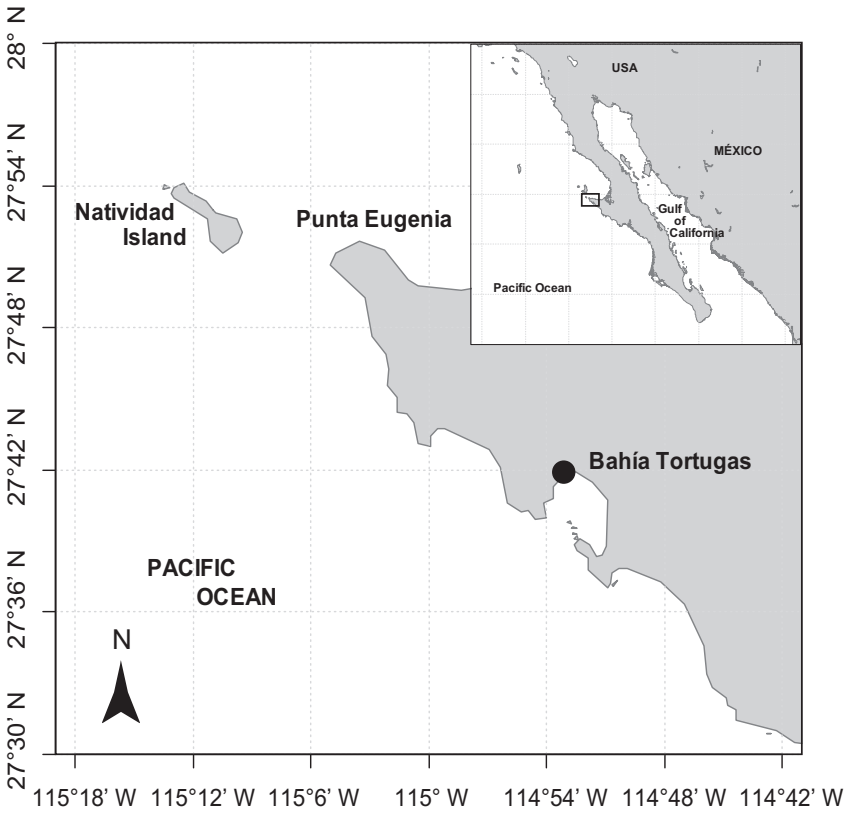

Fig. 1. Location of sampling site in Bahía Tortugas, Baja California Sur, Mexico.

related to human exposure (diet) criteria.

2. Material and methods

2.1. Sample collection

Elasmobranchs samples were collected in March–April, August–September and November of 2014 in Bahía Tortugas (27° 39′35″N; 114° 52′35″W) located on the west coast of Baja California Sur, Mexico (Fig. 1). Specimens were captured by local fishermen using gill nets and all individuals collected were commercially sold for human consumption. Size (total length for the shovelnose guitarfish and the banded guitarfish, and disc width for the bat ray) and sex were recorded for each individual. Sexual differentiation was determined by the presence of claspers in males. For each specimen, between 5 and 30 g of muscle (dorsal side near the head) and liver tissue were collected and placed in plastic bags. Occasionally, organisms were collected from the net lacking internal organs, in which case muscle and liver matched samples were unavailable. All samples were kept on ice in coolers and transported to the laboratory at Centro Interdisciplinario de Ciencias Marinas del Instituto Politécnico Nacional (CICIMAR-IPN, La Paz, BCS, Mexico) and stored frozen (− 20 °C).

In the laboratory, all tissues were sub-sampled (range 2–20 g each) using a clean stainless steel scalpel and stored at − 20 °C in acid-washed plastic containers. Samples were freeze-dried (Labcono, FreeZone 2.5 Liter) for 24–48 h as described by Cyr et al. (2016) and homogenized using a porcelain mortar and pestle cleaned between samples with HCl acid at 10% and distilled water. Weight of each sample before and after freeze-drying was determined to calculate the percent water in each tissue once a consistent mass was achieved (fully dried).

2.2. Total mercury concentration ([THg]) analysis

The [THg] was determined in the Wildlife Toxicology Laboratory (WTL) at the University of Alaska Fairbanks (UAF) USA, using a direct Hg analyzer (DMA-80, Milestone, Shelton, CT, USA; US EPA method 7473) with thermal decomposition, amalgamation and atomic absorption spectrophotometry, in a manner similar to Cyr et al. (2016). The instrument was calibrated using a 14-point calibration curve ranging from 0.5 to 400 ng THg. The detection limit was 1 ng THg. Samples were freeze-dried for 24 h again before each run to remove any potential residual moisture. Blanks, aqueous standards (10 ng at 0.1 mg kg^{-1}, Perkin-Elmer), and standard reference materials (DORM-4, TORT-2 National Research Council Canada, Ottawa ON, Canada) were analyzed for each analytical run for quality assurance. Measurements of aqueous standards were repeated after every 18 samples. Percent recoveries of standard reference materials and aqueous standards were within 91–109%. All samples were analyzed in triplicate (muscle 16–27 mg, liver 30–41 mg each) and the coefficient of variation for triplicate samples was < 11%.

2.3. Statistical and sexual maturation analysis

Data were grouped by sex and maturity stage for each species of ray as follows: IF = immature female; MF = mature female; IM = immature male; MM = mature male. Maturity stage was assigned according to species morphometric criteria. A disc width for the male of > 62 cm and female of > 88.1 cm are considered mature for the bat ray (Martin and Caillet, 1988); for the shovelnose guitarfish, a total length for the male > 80 cm and a female > 100 cm are considered mature (Downton-Hoffmann, 2007); and a total length for the male > 69 cm and female > 77 cm are deemed mature for the banded guitarfish (Villavicencio-Garayzar, 1995).

Normality and homogeneity of variance were assessed by using Kolmogorov-Smirnov and Bartlett tests. Kruskal-Wallis tests and Mann-Whitney *U* test were used to make statistical comparisons between species for each tissue for each maturation-sex group (e.g., IF of each species). To determine in which species [THg] differed within each group, multiple comparisons of mean ranks for all groups were used. Wilcoxon matched pairs test was used to detect differences in [THg]