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Mercury, arsenic, cadmium and lead in two commercial shark species (*Sphyrna lewini* and *Caraharinus porosus*) in Trinidad and Tobago

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ABSTRACT

Sharks are long-lived apex predators which can accumulate toxic metals such as mercury and arsenic. Samples of *Sphyrna lewini* and *Carcharinus porosus* were collected from two commercial fish landing sites in Trinidad. Heavy metal concentrations were determined in the muscle, dorsal fin, vertebrae and liver using atomic absorption spectrometric. The provisional tolerable weekly intake (PTWI) and target hazard quotient (THQ) were determined to assess the potential health risks to consumers. Mercury levels ranged between 74–1899 μg/kg in *S. lewini* and 67–3268 μg/kg in *C. porosus.* Arsenic levels ranged between 144–2309 μg/kg in *S. lewini* and 762–6155 μg/kg in *C. porosus.* Cadmium levels generally ranged between 0.27–27.29 mg/kg in *S. lewini* and 0.6–29.89 mg/kg in *C. porosus.* Lead levels generally ranged between 0.14 and 208.81 mg/kg in *S. lewini* while *C. porosus* levels ranged between 0.30 and 459.94 mg/kg. The PTWI and THQ values suggest that consumption of these shark species can therefore be a major source of exposure to lead, cadmium, arsenic and mercury in humans and is likely to have potential health risk over long term exposure.

Heavy metals are of global concern because of their high toxicity, potential to accumulate through food webs and the significant health risk they pose upon ingestion. Sharks, which are long-lived, apex predators, occupy the highest trophic levels in the marine environment and can efficiently bioaccumulate heavy metals to levels which may exceed the safe limits for human consumption. For example, in 1991, the Florida Department of Health and Rehabilitative Services issued fish advisories recommending limited consumption of sharks after investigations found that they contained high levels of Hg (3.9 mg/kg) (Florida Department of Health and Rehabilitative Services, 1991). Furthermore, the Florida Department of Health (FDOH) currently advises that women of childbearing age and young children should not consume shark while others should not eat large sharks (> 109 cm) and limit consumption of smaller sharks to one meal per month (FDOH, 2013). Mercury, cadmium and lead levels in shark tissues have been previously reported (Glover, 1979; Cornish et al., 2007; Bosch et al., 2016; Hueter et al., 1995; Storelli et al., 2003; Garcia-Hernandez et al., 2007; Evers et al., 2008) in various studies. However, fewer studies have focused on arsenic contamination in sharks and other marine species (Hanaoka et al., 1986; USEPA, 1997; Storelli et al., 2005; Falcoä et al., 2006; Gutiérrez-Mejía et al., 2009). Arsenic levels in marine organisms can vary widely, but typical levels range between 1 and 100 μg As g^{-1}. However, despite high levels of total arsenic in seafood, ingestion of seafood is not easily linked to arsenic toxicity in humans (Edmonds and Francesconi, 1993). Consumption of low levels of arsenic can increase the risk of cancer; therefore it is still worthwhile to consider the potential long term cancer risk since ingestion of seafood may lead to the generation of metabolites involved in arsenic-induced carcinogenesis. Other metals such as cadmium and lead have no biological importance in organisms and can also have toxicological effects on kidneys, bone and nervous systems.

Seafood consumption has changed significantly over the past four decades. Global fish consumption has increased from 9.6 kg per capita in the 1960′s to 15 kg per capita in 2011. In 2016, global consumption exceeded 20 kg per capita, an increase that was attributed to increased supplies from aquaculture and improved fisheries management. Fish consumption rates in Caribbean countries typically range between 10 and 60 kg per capita, with many of the islands (Anguilla = 49.5 kg; Antigua and Barbuda = 55.2 kg; Barbados = 40.6 kg; Grenada = 44 kg; St Lucia = 32.5 kg) having consumption rates above the 2011 global average (15 kg per capita) (FAO, 2013).

The most common fish species consumed in the region include; *Scomberomorus brasiliensis*, *Scomberomorus cavalla*, *Lutjanus purpureus* and *Micropogonias furnieri*. Sharks are not readily consumed except in a few countries such a Trinidad and Tobago where consumption rates are typically high. Trinidad and Tobago captures about 488 tonnes of shark

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each year, most of which is consumed locally. The most common species are *Carcharnihus limbatus* (black fin), *Sphyrna lewini* (hammer head) and *Carcharinus porosus* (poppy shark) because they are perceived to have excellent organoleptic qualities. Presently there are no reports on metal contamination in sharks from the Caribbean region, or the potential health risk to consumers. However, some studies have reported probable health risk which may be linked to seafood consumption (Neupane, 2010; Pinto Pereira and Teelucksingh, 2009). Both these studies focused on mercury contamination and recommended that further studies needed to be conducted to assess the level of mercury in fish consumed in Trinidad and Tobago. This study investigates the levels of heavy metals (Hg, As, Pb and Cd) in two shark species; *Sphyrna lewini* and *Carcharinus porosus* and the potential health risk to consumers.

A total of 22 specimens [*Sphyrna lewini* (10) and *Carcharinus porosus* (12)] were collected from two fish landing sites at Maracas (north coast of the island), and San Fernando (west central coast of island) in Trinidad. *Sphyrna lewini* samples ranged between 81 and 135 cm (total length), while *Carcharinus porosus* samples ranged between 53 and 62 cm (total length). Each shark was washed with deionized water and immediately dissected to obtain samples of the hypaxial and epaxial muscles, liver, vertebra and dorsal fins. These samples were stored in a freezer at − 20 °C until further analysis for mercury, arsenic, lead and cadmium.

Muscle and fin were thawed and the skin removed. Muscles, connective tissue and blood vessels were also removed from the vertebra which was then dried at 60 °C for 12 h. Aliquot 0.5 g of homogenised samples was pre-digested with 10 mL of analar grade nitric acid. Samples were further digested at 125 °C for 4 h, filtered through a Whatman No. 541 filter paper and diluted to 50 mL (Evans et al., 2010). Mercury analysis was done using cold vapour atomic absorption spectrometry, while lead and cadmium were analysed using flame atomic absorption spectrometry. Aliquot 5 mL of the initial filtrate was diluted to 25 mL with 1% KI solution in 1 N HCL and allowed to stand for 1 h, a process that converts As (V) into As (III) which forms the stable hydride. Arsenic levels was then determined by Hydride generation atomic absorption spectrometric (HGAAS).

The analysis for Hg, As, Pb and Cd was conducted using a varian AA800 atomic absorption spectrophotometer with a VGA 77 vapour generation accessory, a quartz mercury flow thru cell for mercury determination and a hydride absorption cell for arsenic determination. A 25% w/v $SnCl_2$ in 20% w/v HCL solution was used as the reductant for mercury analysis. For arsenic analysis, the reductant used was 0.6% w/v $NaBH_4$ made up in 0.5% w/v NaOH. A quality control sample, the DORM-3 (Dogfish Muscle) Certified Reference Material (National Research Council Canada) was analysed concurrently with the samples and percentage recovery determined for data validation. Precision was established by the use of % Relative Standard Deviation (%RSD) (Table 1). The recoveries ranged between 91.5%–103.9% and showed quantitative agreement with the Certified Values, thus validating the accuracy of the procedure. The %RSD ranged from a low of 1.95% to a high of 3.16% which shows good precision. Additionally, nine sample blanks were also analysed concurrently with the samples and used to establish the method detection limit (MDL).

The provisional tolerable weekly intake (PTWI) is the acceptable level of toxic metal that can be ingested on a weekly basis. The weekly designation is used to stress the importance of limiting intake for potentially toxic substances over a period of time. The PTWI guideline recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) shows appropriate safe exposure levels to estimate the amount of contaminants ingested over a lifetime without appreciable risks. The recommended PTWI guideline for MeHg is 1.6 μg/kg BW (JECFA, 2011). The PTWI values for the intake of the various metals per kg body weight per week could be calculated using the formula:

$$\frac{\text{Amount of fish consumed per week (kg/week)} \times \text{metal concentration in the fish ingested (μg/kg)}}{\text{kg body weight}}$$

The target hazard quotient (THQ) was determined based on the protocol by Chien et al. (2002):

$$THQ = \frac{E_F E_D F_{IR} C}{R_{FD} W_{AD} T_A} \times 10^{-3}$$

where E_F is exposure frequency (estimated at 52 days/year); ED is the exposure duration (70 years) equivalent to the average lifetime; F_{IR} is the food ingestion rate (272 g/person/day); C is the metal concentration in the food (μg/g); R_{FD} is the oral referencedose (Hg = 5.0×10^{-4} μg/g/day; As = 3.0×10^{-4} μg/g/day; Cd = 0.001 μg/g/day; Pb = 0.004 μg/g/day); W_{AB} is the average body weight (60 kg for adult) and T_A is averaging exposure time for non-carcinogens (52 days/year x number of exposure years) (Wang et al., 2005; Amirah et al., 2013).

The range of metal concentrations in the different tissues from each species is shown in Table 2. Lead and cadmium levels were generally highest in each species, followed by mercury and arsenic. The concentration of mercury and arsenic in both *S. lewini* and *C. porosus* were significantly lower than lead and cadmium ($P < 0.05$) for all tissue types (Table 2). Concentrations of cadmium and lead were high in all tissue types for both species (Table 2). Cadmium levels generally ranged between 0.27 and 27.29 mg/kg in *S. lewini* while levels in *C. porosus* ranged between 0.6 and 29.89 mg/kg (Table 2). Lead levels generally ranged between 0.14 and 208.81 mg/kg in *S. lewini* while *C. porosus* levels ranged between 0.30 and 459.94 mg/kg (Table 2). The concentration of lead and cadmium were significantly higher ($P < 0.05$) in the vertebra [*S. lewini* (Cd: 6.19–27.29 mg/kg; Pb: 51.43–208.81 mg/kg) and *C. porosus* (Cd: 7.96–29.89 mg/kg; Pb: 70.92–459.94 mg/kg)] than in the other tissue (epaxial, hypaxial, dorsal fin and liver). Both these metals can be sequestered through biomineralization and stored in calcareous matrix in boned and shells. Levels of lead were also significantly higher than cadmium in the epaxial, hypaxial and dorsal fins (Table 2). There was no significant difference in the metal concentrations between both species (Table 2).

Mercury and arsenic levels were significantly lower ($P < 0.05$) than lead and cadmium in all the tissues (Table 2). The concentration of total mercury ranged between 74.0 and 1899.3 μg/kg in *S. lewini* and 67.3–3268.0 μg/kg in *C. porosus.* These values were similar to those reported for other shark species from various parts of the world (Table 3). Mercury levels were significantly higher ($P < 0.05$) in the hypaxial and epaxial muscle tissue (*S. lewini*, 208.2–1899.3 μg/kg (hypaxial): *C. porosus*, 120.3–3328.1 μg/kg (hypaxial and epaxial)) and dorsal fin (*S. lewini*, 301.6–1466.8 μg/kg: *C. porosus*, 67.3–2368.4 μg/kg) than in the vertebra (*S. lewini*, 54.2–274.1 μg/kg: *C. porosus*, 109.9–1425.2 μg/kg) and liver (*S. lewini*, 74.0–476.7 μg/kg:

Table 1
Average recoveries from Certified Reference Material ($N = 6$) DORM-3.

Element	Certified value (μg/kg)	Measured value (μg/kg)	%Recovery	Precision (% RSD)	MDL (μg/kg)
Mercury	382.00 ± 60.0	397.16 ± 7.71	103.97 ± 3.25	3.12	0.17
Arsenic	6880 ± 300.0	6511.91 ± 217.44	94.65 ± 1.76	3.16	0.21
Cadmium	290.0 ± 20.0	265.48 ± 5.67	91.54 ± 3.38	1.95	0.90
Lead	395.0 ± 50.0	389.40 ± 12.28	98.58 ± 1.16	3.11	2.20