CONCENTRATIONS AND EXPOSURE ASSESSMENT OF TOTAL AND METHYL MERCURY VIA SHARK CONSUMPTION COLLECTED FROM OFFSHORE AND COASTAL WATERS OF KOREA

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Introduction

Mercury (Hg) is a ubiquitous contaminant in the environment with natural sources and anthropogenic activities such as the burning of fossil fuels and mining[1].Once Hg is deposited in aquatic environments, this can be methylated by microorganisms (e.g., sulfate-reducting bacteria) in anoxic conditions to form methlymercury (Me-Hg)[2]. Me-Hg is the most toxic form of Hg and bioaccumulates and biomagnifies in the aquatic food web[3]. Me-Hg has adverse health effects on neurodevelopment damage and immun system alteration, particularly during prenatal exposure[4]. Fish consumption is the major exposure pathway of Hg to general population[5]. Sharks are one of top predator fish in aquatic food web and particularly tend to accumulate significant levels of mercury and Me-Hg in tissues[6]. Sharks are consumed as shark fin soup, fillet, bond and liver oil to human in many countries such as Australia, China, Japan and Korea. The United States Food and Drug Administration (US FDA) designated shark as one of high mercury-containing fishes, which are hazardous to children and pregnant women[7]. Despite of this, very limited data are available on residue levels and exposure to Hg for Korean populations. In the present study, we determined the current residue levels and accumulation features of total mercury (T-Hg) and Me-Hg in 13 shark species from offshore (Indian and Pacific Ocean) and Korean coastal waters. Confounding biological factors such as body size and lipid content were investigated to understand the bioaccumulation of Hg in various shark species. Considering shark consumption in Korea, the daily intake of Hg was estimated to assess potential health risks with a comprison of guidelines from international authorities.

Materials and methods

Thirteen shark species (n = 103) were collected from offshore (Indian and Pacific Ocean) and Korean coastal waters between July and October 2010. After removing the skin of shark, the muscle tissues were homogenized with an ultra-disperser. To determine T-Hg, freeze-dried shark sample (100 mg) was placed on a layer of a mixture of sodium carbonate and calcium hydroxide in a ceramic boat. The sample was then covered with a layer of an additive M. A layer of aluminium oxide was placed over the additive M and then re-covered with a layer of additive M. The boat was transferred into the mercury analyzer for analysis. To determine Me-Hg, freeze-dried shark sample (2 g) was put into a 100 mL-centrifuge tube, and then 10 mL of 25% sodium chloride were added. After shaking, 15 mL of toluene and 4 mL of hydrochloric acid were added. The mixture was then centrifuged, and the organic layer was put into a 125 mL separating funnel. The extract was then washed with 10 mL of 25% NaCl. Five millilitres of L-cysteine solution were added to the extract and shaken for 10 min. After standing for 10 min, the upper layer was put into a 15 mL test tube. After an addition of 4 mL of 75% HCl solution and 5 mL of toluene, the mixture was shaken and centrifuged at 2500 rpm. The toluene layer was separated and dehydrated with anhydrous sodium sulfate. The extracts were concentrated to 1 mL and analyzed by GC/ECD (Agilent GC 6890N). For the determination of lipid content in seafood samples, the freeze-dried samples (3 g) were extracted with 150 mL of hexane in an automatic extraction unit, and lipid content was measured gravimetrically. Detailed preparation and instrumental analyses of T-Hg and Me-Hg have reported from previous study[8].

Results and discussion:

Residue levels of T-Hg and Me-Hg in various sharks

The concentrations of T-Hg and Me-Hg in 13 shark species collected from offshore (Pacific and Indian Ocean) and Korean coastal waters are summarized in Table 1. The concentrations of T-Hg and Me-Hg ranged from 0.11 to 5.12 (mean: 1.40) mg/kg wet weight (ww) and from 0.08 to 3.68 (mean: 1.15) mg/kg ww, respectively. The highest concentration of T-Hg (3.15 ± 0.32 mg/kg ww) and Me-Hg (2.54 ± 0.19 mg/kg ww) was found for shortfin mako shark, followed by blue shark, smooth hammerhead and pelagic thresher shark. In particular, shortfin mako shark, blue shark and smooth hammerhead are known as aggressive feeding species. In addition, the blue shark is deep-sea fish living below over 300 m depth. The Korea Food and Drug Administration

(KFDA) proposed the safty limits of 1.0 mg/kg of Me-Hg for predatory fish including sharks. Fifty-two percentage of shark samples exceeded the threshold level of Me-Hg suggested by KFDA, implying a potential risk by the consumption of sharks in Korea. The concentrations of Me-Hg in the 13 shark species measured in this study were lower than or similar to those reported for sharks from Mediterranean Sea (blacktip shark: 2.67 ± 1.25 mg/kg ww)[9] and higher than Atlantinc Ocean (blacknose shark: 0.53 ± 0.13 mg/kg ww)[10]. Spearman's rank correlation analysis was performed between Hg in dorsal and ventral muscle of shark, to investigate the suitability of taget tissues for monitoring of Hg in sharks. T-Hg and Me-Hg in sharks were significantly correlated between both tissues for all of the shark species, suggesting that Hg have homogenous distribution between tissues of sharks (Fig 1).

Table1. Concentrations (mg/kg wet weight) of Me-Hg and T-Hg, and biological factors of shark species from offshore (Indian and Pacific Ocean) and Korean coastal waters

Species	n[a]	Body length (cm)	Body weight (kg)	Lipid (%)	T-Hg	Me-Hg	% Me-Hg
Blacktip reef shark	26	90 ± 16	21 ± 11	4.2 ± 1.3	1.05 ± 0.02	0.91 ± 0.03	86.2 ± 7.11
Spiny dogfish	17	81 ± 8.2	2.7 ± 0.9	18 ± 3.6	1.08 ± 0.02	0.89 ± 0.001	82.9 ± 5.74
Blue shark	15	112 ± 20	22 ± 8.2	3.5 ± 1.5	2.44 ± 0.38	1.94 ± 0.13	79.9 ± 8.97
Pelagic thresher shark	13	96 ± 27	40 ± 29	4.4 ± 2.1	1.56 ± 0.11	1.35± 0.06	85.4 ± 6.21
Shortfin Mako shark	7	118 ± 9.8	44 ± 26	4.3 ± 1.4	3.15 ± 0.10	2.54 ± 0.19	81.3 ± 5.73
Cloudy catfish	5	33 ± 2.9	0.8 ± 1.0	4.8 ± 3.4	1.12 ± 0.10	0.85 ± 0.07	75.0 ± 7.89
Oceanic Whitetip shark	3	88 ± 30	17 ± 16	4.7 ± 0.7	0.53 ± 0.01	0.39 ± 0.05	78.3 ± 11.9
Shortnose spurdog	4	87 ± 2.9	4.2 ± 0.7	3.4 ± 2.1	0.15 ± 0.01	0.12 ± 0.01	73.6 ± 7.51
Milk shark	3	107 ± 12	9.6 ± 0.7	4.4 ± 2.0	0.18 ± 0.01	0.13 ± 0.01	69.9 ± 10.6
Smooth hammerhead	3	105 ± 17	17 ± 12	4.5±0.3	1.65 ± 0.10	1.42 ± 0.04	81.9 ± 11.9
Banded houndshark	3	111 ± 40	5.7 ± 3.2	4.6±1.0	0.96 ± 0.16	0.68 ± 0.15	68.9 ± 5.32
Crocodile shark	2	76 ± 0.7	1.6 ± 0.4	4.4 ± 0.8	1.44 ± 0.03	1.06 ± 0.03	73.0 ± 2.03
Starspotted smooth-hound	2	60	1.6 ± 0.8	6.0 ± 1.0	0.32 ± 0.04	0.24 ± 0.01	73.6 ± 5.58

[a] Number of samples.

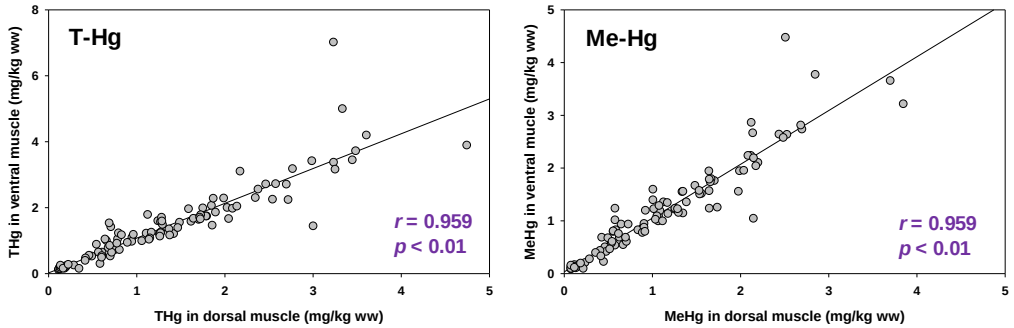

Fig 1. Relationship between concentrations of T-Hg and Me-Hg in dorsal and ventral muscle of sharks

Associations with biological factors

Spearman's rank correlation analysis was performed between concentrations of Me-Hg in sharks and their biological factors (Fig 2). The concentrations of Me-Hg in sharks were significantly correlated with their body length ($r = 0.473$, $p < 0.01$) and weight ($r = 0.474$, $p < 0.01$), indicating that the body size is an essential confounding factor on the bioaccumulation of Hg in most of shark. This is consistent with an earlier study for shark[11]. Previous studies reported no significant correlations between body size and the OC levels in shark[12]. Our results indicate that pollutants are differently distributed in shark depends on chemical properties. In contrast, lipid content ($r = -0.100$, $p = 0.315$) was not significantly correlated with the concentration of Me-Hg in any shark species.

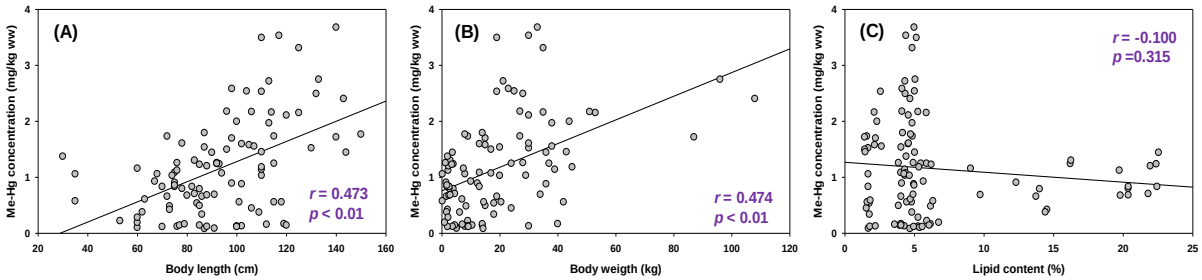

Fig 2. Correlations between concentration of Me-Hg and (A) body length (cm), (B) body weight (kg) and (C) lipid content (%) in various sharks.

Estimated daily intakes of Me-Hg and T-Hg associated with shark consumption

The estimated daily intakes (EDI) of T-Hg and Me-Hg via shark consumption to the Korean population are presented in Fig 3. (A). The EDI of Me-Hg through the shark consumption by Korean population were compared with safty limits from international authorities. The Joint FAO-WHO Expert Committee on Food additives (JECFA) established a provisonal tolerable weekly intake (PTWI) of 1.6 μg/kg body weight (bw)/week, corresponding to 0.23 μg/kg bw/day for MeHg[13]. The United States Environmental Protection Agency (US EPA) also proposed 0.1 μg/kg bw/day as reference dose (RfD) for Me-Hg[14]. In the present study, the intakes of average Me-Hg for Korean population (1.42 μg/kg bw/day) was much higher than the levels suggested in the JECFA and US EPA. The maximum allowable consumption limit daily intakes of Me-Hg associated with shark consumption for the Korean population are presented in Fig 3. (B). Our results emphasize the health risks resulting from shark consmption, except for few shark species. Considering traditional diet habit of sharks in Korea, continous monitoring and exposure assessment should be instituted to protect human health from the exposure of Hg.

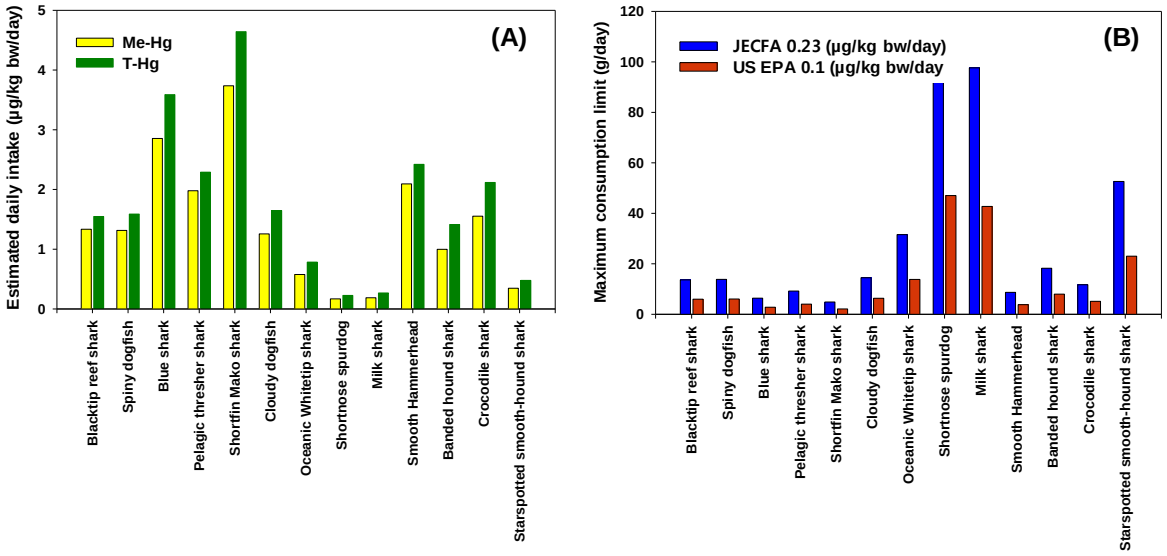

Fig 3. (A) Estimated daily intakes of T-Hg and Me-Hg in 13 shark species to general population in Korea and (B) Maximum allowable consumption limit (g/day) for 13 shark species for guidelines from the JECFA and US EPA.

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