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Baseline

Factors affecting mercury concentrations in two oceanic cephalopods of commercial interest from the southern Caribbean

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ABSTRACT

Mercury (Hg) concentrations have significantly increased in oceans during the last century. This element accumulates in marine fauna and can reach toxic levels. Seafood consumption is the main pathway of methylmercury (MeHg) toxicity in humans. Here, we analyzed total Hg (T-Hg) concentrations in two oceanic squid species (*Ommastrephes bartramii* and *Thysanoteuthis rhombus*) of an increasing commercial interest off Martinique, French West Indies. Stable isotope ratios reveal a negative linear relationship between $\delta^{15}N$ or $\delta^{13}C$ in diamondback squid samples. No significant trend was observed between $\delta^{34}S$ values and T-Hg concentrations, contrasting with the sulfate availability and sulfide abundance hypotheses. This adds to a growing body of evidence suggesting Hg methylation via sulfate-reducing bacteria is not the main mechanism driving Hg bioavailability in mesopelagic organisms. All squid samples present T-Hg levels below the maximum safe consumption limit (0.5 ppm), deeming the establishment of a commercial squid fishery in the region safe for human consumption.

Mercury (Hg) naturally occurs in our planet and may enter the oceans after geogenic emissions from volcanic activity or weathering of rocks (Amos et al., 2013). Notwithstanding, Hg concentrations found in oceans today result mainly from historical and current anthropogenic activities such as gold-mining, waste treatment, and the use of coal-firing power plants (UNEP, 2019). Hg in surface ocean waters less than 200 meter deep has roughly tripled during the last century (~230% increase) (Outridge et al., 2018; UNEP, 2019). In oceanic waters, the vertical distribution of total Hg concentrations follows a similar pattern to that of macronutrients, with concentration increasing with water depth (Lamborg et al., 2014). Thus, concentrations increase in mesopelagic (200–1000 m) and bathypelagic habitats and organisms (Lamborg et al., 2014; Bowman et al., 2015; Sun et al., 2020). With high amounts of Hg entering the oceans and slow deposition rates occurring on the ocean floor (Lamborg et al., 2016), it is critical to improve our understanding on this element's pathways and accumulation in marine organisms, particularly those of commercial interest for human consumption (Amos et al., 2013; Bowman et al., 2020).

Methylmercury (MeHg), an organic form of Hg, biomagnifies through the food web, reaching high concentrations in marine top predators (Liu et al., 2011). MeHg is one of the Hg species known to have detrimental effects in marine organism health including immunotoxicity, visual impairment, inhibited growth, lethargy, and lower reproductive success (Eisler, 1987; Wolfe et al., 1998; Depew et al., 2012; Evers, 2018; Chételat et al., 2020). Due to its bioavailability, the majority of Hg found in edible fish tissue is in the form of MeHg (Watanabe et al., 2012). Hg exposure through seafood consumption is considered a global toxicity issue (UNEP, 2013). MeHg poses a health risk for human health with effects ranging from brain and central nervous system damage to fetal cognitive development complications (WHO, 2017).

Hg levels in marine fauna have been described across multiple trophic levels and taxa (e.g. Evers and Sunderland, 2019). Species fished for human consumption have been an important focus of toxicological studies as understanding their Hg levels is beneficial for the wellbeing of both marine organisms and humans as consumers (Bosch et al., 2016; Evers and Sunderland, 2019). Governments and health agencies worldwide have recognized the need to assess the safety of seafood products before making them available for consumers by establishing

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maximum safe consumption limits for Hg and MeHg in seafood such as 0.46 ppm of T-Hg (FDA-US, 2018) and 1.6 μg MeHg/kg bw (potential tolerable weekly intake, WHO, 2008) (see de Almeida Rodrigues et al., 2019 for a detailed review).

Toxicological research on marine fauna also aims at describing biological and ecological factors affecting Hg accumulation (Wiener et al., 2003). Trophic level and food web length have been shown to be positively correlated with higher Hg and MeHg concentrations due to their biomagnifying ability (Kidd et al., 1995; Lavoie et al., 2013). However, the relationship of Hg with other factors such as sex, tissue type, or ontogeny varies for each species considered (Wiener et al., 2003; Evers and Sunderland, 2019). While stable nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) isotopes are commonly used to infer relative trophic levels and foraging habitats, respectively (Post, 2002; McCutchan et al., 2003), sulfur isotopes ($\delta^{34}S$) have rarely been considered, particularly in the open ocean (Carr et al., 2017). $\delta^{34}S$ data can be used to differentiate between consumers feeding on pelagic and offshore environments vs. benthic and coastal food sources (Connolly et al., 2004; Pinzone et al., 2019). This adds resolution to Hg dietary pathways in different marine habitats due to the role of sulfate-reducing bacteria in Hg methylation (Liu et al., 2012; Elliott and Elliott, 2016, Góngora et al., 2018).

Cephalopods include some of the largest marine invertebrates and are important consumers in food webs both as active predators and major prey of upper-trophic level predators such as sharks, tuna, billfishes, and marine mammals (Clarke, 1996; Smale, 1996; Overholtz et al., 2000; dos Santos and Haimovici, 2002). Historically considered as an unconventional marine resource compared to finfish (Roper et al., 1984; Arkhipkin et al., 2015), only 10 to 14% of squid species are commercially exploited worldwide (Arkhipkin et al., 2015; Aguilera, 2018). These species are muscular, grow fast and have a lifespan of one to two years (Rodhouse et al., 2014). Squids are considered to be one of the few marine resources to have the potential for further commercial exploitation around the globe (Jereb and Roper, 2010; Arkhipkin et al., 2015). Two species identified as of interest for commercial fisheries globally are the neon-flying squid (*Ommastrephes bartramii*, Lesueur, 1821) and the diamond-back squid (*Thysanoteuthis rhombus*, Troschel, 1857) (Jereb and Roper, 2010; Rodhouse, 2005; Rodhouse et al., 2014; Arkhipkin et al., 2015).

The neon-flying squid belongs to the Ommastrephid family, which is considered the most economically important squid group in commercial fisheries worldwide (Jereb and Roper, 2010; Rodhouse et al., 2014; Fernández-Álvarez et al., 2020). This species is the second largest of the family reaching 42 cm in mantle length (ML) for males and 90 cm ML for females (Jereb and Roper, 2010). Known to be circumglobally distributed in subtropical and temperate waters (Jereb and Roper, 2010), the structure of populations is still not fully understood across ocean basins (Fernández-Álvarez et al., 2020) . The diamondback squid is the only species within the genus *Thysanoteuthis*. Males and females both reach a maximum size of 100 cm ML (Jereb and Roper, 2010). This oceanic squid inhabits tropical and subtropical regions around the globe (Jereb and Roper, 2010) and its exploitation for human consumption started in Japan in 1962 (Bower and Miyahara, 2005). In the early 2000s, the fishing techniques developed by the Japanese, known as "Taru-nagashi", were implemented in the Caribbean Sea (Herrera et al., 2011). The first effective diamondback squid fishery in the region started in 2001 in Dominican Republic (Herrera-Moreno, 2005; Herrera et al., 2011). The Secretariat of Coastal and Marine Resources has stated that the diamondback squid could become one of the most important marine resources in the region (Herrera-Moreno, 2005). The spread of small-scale fishing activities to Tobago in 2004, Jamaica in 2005, and Dominica in 2012 is indicative of growing commercial interest on this species (Pau, 2018).

Important squid fisheries exist for the longfin squid (*Doryteuthis pealeii*), arrow squid (*Doryteuthis plei*), brief squid (*Lolliguncula brevis*), and southern shortfin squid (*Illex coindeti*) in the Caribbean Sea (Judkins et al., 2009). However, both the neon-flying squid and the diamondback squid are poorly exploited in the region (Rodhouse, 2005). Martinique (French West Indies) is located in the southeastern Caribbean Sea, and does not commercially exploit these two species but interest in their economic potential is growing (Pau, 2018). Efforts to better determine the distribution of the species and increase fishing efficiency have been carried out by the Regional Committee for Maritime Fisheries and Marine Farming in Martinique (Pau, 2018).

Here, we report the total Hg levels (T-Hg) found in mantle tissue samples of the neon-flying squid and the diamondback squid collected off Martinique. Our results serve to inform French authorities about possible toxicological risks associated with these emerging squid fisheries. Further, we explore allometric relationships between Hg concentrations, length and body mass of the squids and reveal the value of ecological tracers in understanding Hg accumulation patterns in oceanic cephalopods.

Sampling for neon flying squids and diamond back squids took place around the island of Martinique (14.6415° N, 61.0242° W) between December 2016 and February 2017, and between October 2017 and March 2018. Fishing surveys were carried out as part of an exploratory study led by the Regional Committee for Maritime Fisheries and Marine Farming. A total of 27 sampling trips were completed aboard small artisanal fishing boats (<10 m) following similar squid fishing techniques to the ones employed by the Japanese ("Taru-nagashi", Jereb and Roper, 2010). Essentially, longlining with jigs occurred during daytime hours at depths ranging from 300 to 600 m deep, with the majority of areas presenting a bathymetric profile of 1000 m (from 600 to 2500 m deep). Seven lines were deployed at four different depths: one line at 600 m, 400 m and 300 m, and four lines at 500 m.

Once caught, squids were gaffed in the water and stored in a cooler with ice. Upon return to land individuals were identified to the species level using visual identification guides (Roper et al., 1984). Preliminary sex identification was performed visually by inspecting the buccal membrane. Sex was later confirmed by observing the gonads after evisceration. Mantle measurements were taken for all individuals and a subset of mantle samples were obtained for stable isotope and Hg analyses.

Isotopic ratios of N, C and S were measured as described in Pinzone et al. (2015) and are hereafter expressed in delta (δ) notation in parts per thousand (‰). The isotopic ratios were estimated relative to international standards such as Vienna Pee Dee Belemnite (VPBD) for carbon, Atmospheric Air for nitrogen and Vienna Canyon Diablo Troilite (VCDT) for sulfur. We used International Atomic Energy Agency (IAEA, Vienna, Austria) certified reference materials calibrated against the international isotopic references sucrose (IAEA-C6, $\delta^{13}C = -10.8 \pm 0.5‰$; mean ± SD), ammonium sulfate (IAEA-N2, $\delta^{15}N = 20.3 \pm 0.2‰$; mean ± SD) and silver sulfide (IAEA-S1, mean $\delta^{34}S = -0.3‰$) as primary standards, and sulfanilic acid ($\delta^{13}C = -28.3 \pm 0.08‰$; $\delta^{15}N = -0.82 \pm 0.25‰$; $\delta^{34}S = -1.34 \pm 0.16‰$; mean ± SD in each case) as secondary analytical standard. Samples were analyzed using an IRMS (IsoPrime100, Isoprime, U.K.) coupled in continuous flow to an elemental analyzer (EA, vario MICRO cube, Elementar, Germany). Replicability of the secondary analytical standard was 0.2‰ for $\delta^{15}N$ and $\delta^{13}C$, and 0.3‰ for $\delta^{34}S$.

Total Hg (T-Hg) concentrations were determined following the protocol reported in Pinzone et al. (2019). Briefly, dried mantle samples (~0.01 g) were accommodated in quartz boats (Volume: 1500 μL) prior to their analysis. The T-Hg content was determined using atomic absorption spectrometry at 254 nm, in a Direct Mercury Analyzer (DMA 80 Milestone, Minnesota, USA) according to the US EPA standard method 7473 and expressed in ng/g dry weight (dw). Quality assessment was operated through the use of replicates, standards (100 ng T-Hg g), blanks (HCl 1%) and reference samples (DOLT-3 Dogfish liver, T-Hg = 3370 ± 140 ng/g dw and DORM-2 Dogfish, muscle = 4640 ± 140 ng/g dw) at the beginning and the end of each series. Recovery of the reference materials was 87–110% and 80–107% for DORM-2 and DOLT-3 respectively. MeHg was not directly assessed in this study but it has previously been reported that 68–99% of T-Hg in mantle tissue of squid and other cephalopods is in the form of MeHg (Bustamante et al., 2006; Raimundo et al., 2010, 2014; Cardoso et al., 2012; Anual et al., 2018). T-Hg levels will be presented in wet weight (ww). The ww/dw ratio was calculated for each sample, weighting the mantle tissue before and after freeze-drying for 24 h. The mean ww/dw ratio was 5.2 (N = 7) for the neon-flying squid, and 4.10 (N = 24) for the diamondback squid.

During fishing surveys, 268 longlines were deployed with an average drift time of 4 h and 22 min. A total of 114 longlines were set off the Atlantic coast, 96 along the Caribbean coast, and 41 and 17 in the Saint Lucia and Dominica channels respectively. In total, 58 individuals were caught (n = 49 diamondback and n = 9 neon flying squid). The majority of the catches (n = 36) occurred off the Atlantic. Neon-flying squids were only found in the Atlantic and the Saint Lucia channel. Thirty-one samples (Fig. 1) were obtained for stable isotope and T-Hg analyses, 24 from diamondback squids, and 7 neon flying squids. Due to the low sample size of neon-flying squids and the non-normality of the data obtained, non-parametric tests were performed using R software (Version 3.5.2, R Core Team, 2018).

Squid sizes varied from 33 to 81 cm in mantle length and from 1.3 to 16.3 kg of body mass (Table 1). Diamondback squids were significantly larger in length and body mass than neon flying squids (Mann–Whitney–Wilcoxon test, W = 161, $p < 0.0001$ and W = 158, p = 0.0002 for body mass and length respectively). Stable isotope analyses revealed no differences in $\delta^{15}N$, $\delta^{13}C$, or $\delta^{34}S$ values between squid species (Mann–Whitney–Wilcoxon test, W = 81, W = 119 and W = 109 for $\delta^{15}N$, $\delta^{13}C$, or $\delta^{34}S$ respectively; all p-values >0.05, Table 2). When only diamondback squids are considered, a significant linear relationship exists in which higher $\delta^{15}N$ values are observed at lower $\delta^{13}C$ value (R = 0.67, p = 0.001, Fig. 2).

T-Hg concentrations were normally distributed for the diamondback squid but not for the neon flying squid (Kolmogorov-Smirnov normality test, $p < 0.0001$, Shapiro-Wilkinson test, p = 0.039). Hg values significantly differed between both species (Mann–Whitney–Wilcoxon test, p = 0.017), with higher concentrations for the neon-flying squid (210±157 μg/kg ww, Table 2). The diamondback squid concentrations averaged 101±22 μg of Hg/kg ww. Wet mass to dry mass ratios were 4.10±0.26 and 5.20±0.78 for the diamondback and the neon-flying squids, respectively. Annual and seasonal variation were evaluated for the diamondback squid. No significant differences were found in T-Hg concentrations or body mass of the individuals caught between years (p-value = 0.9 and 0.42 for T-Hg and body mass respectively, *t*-test) or seasons (p-value = 0.96 for T-Hg, ANOVA, and 0.59 for body mass, Kruskal-Wallis).

Table 1
Number of samples obtained per species (n), specifying the amount of samples of each sex (n_{MALES} and $n_{FEMALES}$) per species, mean, minimum, and maximum mantle length (ML) and body mass expressed in cm and kg respectively. Mean ML and body mass ± SD.

Species	Diamondback squid	Neon-flying squid
n_{TOTAL}	24	7
n_{MALES}	14	0
$n_{FEMALES}$	10	7
ML (cm)	74.09±6.01	46.29±9.52
Min ML (cm)	58.00	33.00
Max ML (cm)	81.00	56.00
Body mass (kg)	13.30±2.98	3.96±2.15
Min body mass (kg)	5.40	1.30
Max body mass (kg)	16.30	6.80

Table 2
Isotopic ratios for N, S and C, expressed with δ notation. Results expressed in ‰; mean ± SD. Total Hg results (Hg) expressed in μg/kg ww, mean ± SD and μg/kg dw, mean ± SD.

Species	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)	$\delta^{13}C$ (‰)	Hg dry weight (μg/kg)	Hg wet weight (μg/kg)
Diamondback squid	7.9±0.6	16.9±0.8	−17.8±0.5	412±91	101±22
Neon-flying squid	8.0±0.8	16.4±0.7	−18.5±0.9	1188±1042	210±157

In order to understand the effects of body size and trophic ecology on Hg concentrations, mantle length and body mass separately, combined with $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ values were selected as independent variables for simple and multiple linear regression models (Table 3). Due to the low sample size and non-normality of the neon flying squid results, linear regression models were only used for diamondback squid samples. Overall, body mass and $\delta^{34}S$ values were the only variables that significantly predicted the variation in T-Hg levels in the diamondback squid (p = 0.019, Table 3). The adjusted R^2 value of the multiple linear model including both variables indicate that body mass and $\delta^{34}S$ predict 24.68% of the variation in T-Hg levels in this species, while body mass alone significantly explains 13.25% (p = 0.045, Table 3). Model selection was performed using the Akaike information criterion (AIC), which indicated that the model including both body mass and $\delta^{34}S$ was preferred (ΔAIC > 2, Table 3).

Reports of Hg levels in cephalopods exist for large areas such as the

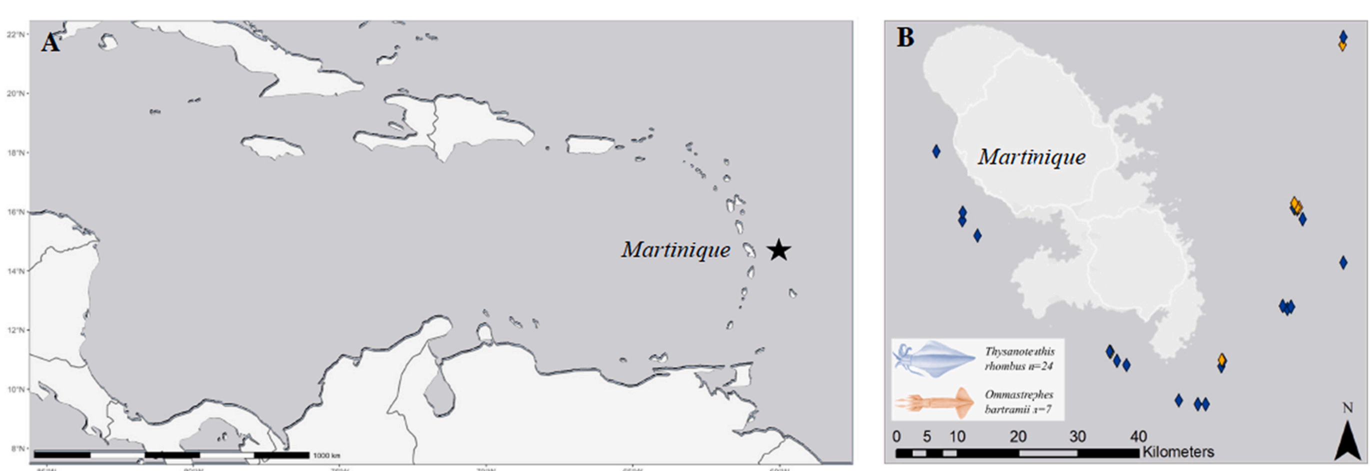

Fig. 1. A) Map of the Caribbean Sea with Martinique marked with a star symbol. B) Map of the island of Martinique with the locations were the squids used for this study (n = 31) were caught. The diamondback squid individuals are represented in blue and the neon-flying squid in orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

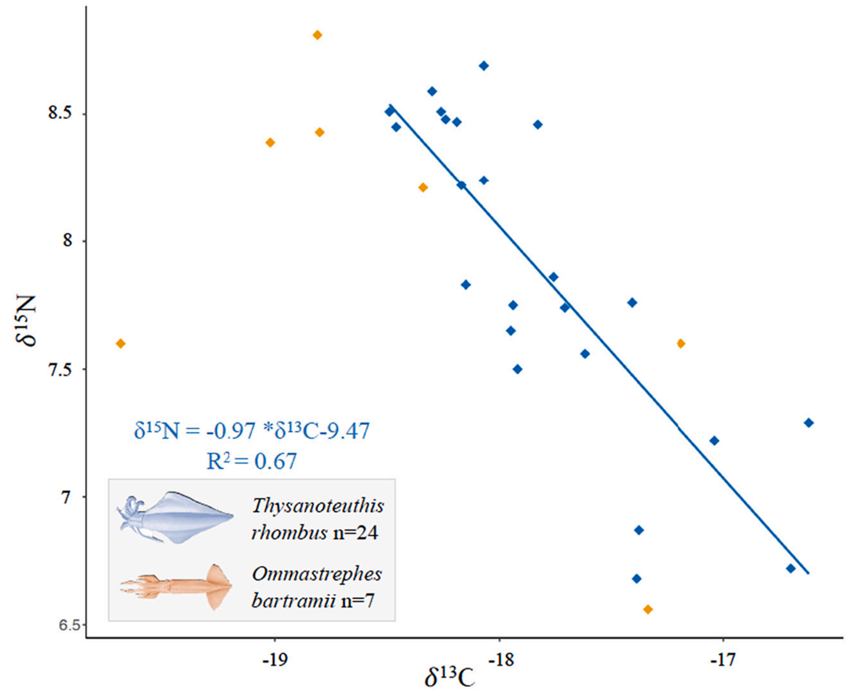

Fig. 2. Relationship between $\delta^{15}N$ or $\delta^{13}C$ values for both squid species. In blue the diamondback squid and in orange the neon-flying squid. Blue line indicates a significant negative linear relationship between $\delta^{15}N$ or $\delta^{13}C$ in diamondback squid samples. Equation and R^2 values provided (in blue) for the aforementioned significant relationship. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Simple and multiple linear regression models for diamondback squid samples with associated p-values and adjusted R^2 values. Significant models marked with (*). AIC values provided for both significant models.

Model	p-Value	Adjusted R^2	AIC
Hg ~ mantle length	0.111	0.074	
Hg ~ mantle length + $\delta^{13}C$	0.283	0.030	
Hg ~ mantle length + $\delta^{15}N$	0.207	0.060	
Hg ~ mantle length + $\delta^{34}S$	0.060	0.169	
Hg ~ body mass	0.045 *	0.133	284.95
Hg ~ body mass + $\delta^{13}C$	0.133	0.096	
Hg ~ body mass + $\delta^{15}N$	0.115	0.109	
Hg ~ body mass + $\delta^{34}S$	0.019 *	0.247	282.44

East China Sea (Kazama et al., 2020), the North-east Atlantic Ocean (Bustamante et al., 2006), and the Southern Ocean (Seco et al., 2020). Regional studies have taken place in numerous localities, including South Korean waters (Nho et al., 2016), South India (Shalini et al., 2020), South-east Australia (Pethybridge et al., 2010), several regions of the Mediterranean Sea (Schuhmacher et al., 1994; Storelli and Marcotrigiano, 1999), and Portugal and the Azores (Monteiro et al., 1992; Lourenço et al., 2009; Cardoso et al., 2012).

One previous report of Hg levels for the neon-flying squid can be found from Azorean waters, in the central North Atlantic Ocean (Monteiro et al., 1992). In this study, 14 neon-flying squids between 10 and 33 cm (mantle length) and ranging from 0.021 to 0.954 kg of body mass were sampled, averaging T-Hg levels of 47 ± 8.3 μg/kg ww (min: 19 μg/kg ww, max: 122 μg/kg ww) (Monteiro et al., 1992). Individual neon-flying squids sampled for our study were notably larger, with minimum mantle length (33 cm) being their largest one and our smallest body mass (1.3 kg) surpassing their heaviest individual. It is therefore not striking that the average T-Hg levels for this species in our study are higher, at 210 ± 156.8 μg/kg ww. However, it is worth noting that, to the best of our knowledge, this is the highest T-Hg average presented for an ommastrephid squid species in the scientific literature (See Penicaud et al., 2017 for review, Lischka et al., 2018; Seco et al., 2020; Minet et al., 2021).

Reports of Hg levels for the diamondback squid are almost inexistent in the literature. However, two muscle samples were identified in the stomach contents of blue sharks (*Prionace glauca*) and averaged T-Hg concentrations of 10 μg/kg ww (Escobar-Sánchez et al., 2011). This value is an order of magnitude lower than the average found in our samples (101±22 μg/kg ww). Direct comparison between results is not possible due to methodological differences. The squid samples from the stomach contents had been partially digested and there is no information on size or weight of the individuals. Nonetheless, knowing North Atlantic waters have higher Hg levels than the North Pacific Ocean (Lamborg et al., 2014; Mason et al., 2017), higher concentrations in our samples were expected.

For the diamondback squid, Hg concentrations were better explained by body mass than mantle length (Table 3). Across cephalopod studies, mantle length and body mass are inconsistent predictors of Hg concentrations (Storelli et al., 2006), and results considerably vary across species. In the North-east Atlantic, only three of ten species studied showed a significant influence of mantle length on Hg concentrations (Bustamante et al., 2006). A similar relationship was not found in eight cephalopod species from Malaysia (Ahmad et al., 2015). However, a number of studies have limited sample sizes, which could be an important limiting factor in detecting significant relationships between Hg concentrations and body sizes o (Barghigiani et al., 2000). Nevertheless, body mass resulted in a better prediction of Hg concentrations for diamondback squids, but our limited sample size (n = 31) might, at least partially, explain this result.

Recently, reporting $\delta^{34}S$ in conjunction with $\delta^{15}N$ has been encouraged in order to gain a mechanistic understanding of Hg methylation in oceanic water columns (Elliott and Elliott, 2016; Góngora et al., 2018). Models suggest sulfur metabolic pathways can be associated with MeHg accumulation in the mesopelagic zone, but there is little evidence of sulfate-reducing bacteria having an important role in Hg methylation in oceanic waters (Fitzgerald et al., 2007; Tada et al., 2020). The sulfate availability hypothesis states that if sulfur-reducing bacteria are to play a key role in Hg methylation, sulfate would act as a limiting factor in the process. This would result in an observable positive trend between $\delta^{34}S$ and Hg concentrations (Elliott and Elliott, 2016; Góngora et al., 2018). On the other hand, if sulfate were not the limiting factor and sulfur-reducing bacteria were still to play a key role in Hg methylation, high sulfide levels would result in a negative trend between $\delta^{34}S$ and Hg concentrations (Elliott and Elliott, 2016, Góngora et al., 2018). In this study, the preferred model includes $\delta^{34}S$, suggesting these values help predict the variation in Hg concentrations for the diamondback squid. A slight positive trend between Hg and $\delta^{34}S$ is observable in the data but it is not statistically significant. Due to the lack of a clear Hg/$\delta^{34}S$ relationship, these results add to the growing body of evidence suggesting Hg methylation via sulfate-reducing bacteria is not the main mechanism for MeHg bioavailability in the mesopelagic layer (Weber, 1993; Fitzgerald et al., 2007; Tada et al., 2020).

Concomitantly, and as expected, $\delta^{34}S$ and $\delta^{13}C$ values indicated that both squid species in Martinique feed in open ocean waters, which is consistent with their habitat preferences described in the Sea of Japan and the Bonin Islands (Bower and Miyahara, 2005), the South-west Atlantic Ocean (Lipiński and Linkowski, 1988) and the central North Pacific Ocean (Watanabe et al., 2004). It also further reinforces the value of $\delta^{34}S$ as an ecological tracer. The species investigated in our study are known to feed within the mesopelagic zone at 500 m deep (Jereb and Roper, 2010), where the dynamics of Hg methylation are not yet fully understood (Blum et al., 2013). The mesopelagic layer is characterized by higher MeHg concentrations than in epipelagic (0–200 m) and bathypelagic waters (>1000 m) (Gill and Fitzgerald, 1988; Choy et al., 2009; Peterson et al., 2015). Since mesopelagic prey can account for an important proportion of the MeHg accumulated by their predators (Le Croizier et al., 2020), it is important to carefully assess the risk of mesopelagic fauna consumption.

The diamondback and the neon flying squids are both species of commercial interest in several regions around the world (Rodhouse, 2005). Unlike other fisheries resources, these two squid species have the potential to be further exploited (Rodhouse, 2005). Results in this study show that both species around Martinique can be safely harvested for human consumption. Being an overseas territorial collectivity of France, the island of Martinique enforces the same maximum Hg levels as the Commission of European Communities. For most fishery products the maximum level permitted is 0.50 mg/kg wet weight T-Hg (EC, 2006). None of the samples of diamondback squid or neon-flying squid were above the set limit. The two largest individuals of neon-flying squid in terms of body mass (5.9 and 6.8 kg) had the closest samples to that limit with 0.46 and 0.41 mg/kg wet weight, respectively. Overall, both squid species are safe for human consumption and have the potential to become a source of protein in Martinique and other southern Caribbean islands.

This study is the first to report the presence of the neon-flying squid in the island of Martinique in the scientific literature. We also describe for the first time the Hg levels of both the diamondback squid and the neon-flying squid in the Northwestern Atlantic Ocean. Stable isotope analyses reveal consistency in the trophic ecology of both squid species in this area compared to past studies in different regions. Additionally, we evidence the importance of analyzing sulfur stable isotopes in order to better understand Hg dynamics in marine fauna that inhabit the mesopelagic layer of the ocean.

CRediT authorship contribution statement

Laura García Barcia - Conceptualization, Methodology, Investigation, Writing - Original Draft, Writing – Review and Editing

Marianna Pinzone - Methodology, Investigation, Data Acquisition and Writing – Review and Editing

Gilles Lepoint - Data Acquisition

Cédric Pau – Sample Collection, Writing – Review and Editing

Krishna Das - Writing – Review and Editing, Resources and Supervision

Jeremy Kiszka – Conceptualization, Writing – Review and Editing and Supervision

Declaration of competing interest

All authors state that, to the best of our knowledge, there are no actual or potential conflicts of interest involved in this paper. That includes any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, our work.

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References

Aguilera, S., 2018. Measuring squid fishery governance efficacy: a social-ecological system analysis. Int. J. Commons 12 (2).
Ahmad, N.I., Noh, M.F.M., Mahiyuddin, W.R.W., Jaafar, H., Ishak, I., Azmi, W.N.F.W., Mokhtar, F.A., 2015. The mercury levels in crustaceans and cephalopods from Peninsular Malaysia. Environ. Sci. Pollut. Res. 22 (17), 12960–12974.
Amos, H.M., Jacob, D.J., Streets, D.G., Sunderland, E.M., 2013. Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. Glob. Biogeochem. Cycles 27 (2), 410–421.
Anual, Z.F., Maher, W., Krikowa, F., Hakim, L., Ahmad, N.I., Foster, S., 2018. Mercury and risk assessment from consumption of crustaceans, cephalopods and fish from West Peninsular Malaysia. Microchem. J. 140, 214–221.
Arkhipkin, A.I., Rodhouse, P.G., Pierce, G.J., Sauer, W., Sakai, M., Allcock, L., Zeidberg, L.D., 2015. World squid fisheries. Reviews in Fisheries Science & Aquaculture 23 (2), 92–252.
Barghigiani, C., Ristori, T., Biagi, F., De Ranieri, S., 2000. Size related mercury accumulations in edible marine species from an area of the Northern Tyrrhenian Sea. Water, air, and soil pollution 124 (1), 169–176.
Blum, J.D., Popp, B.N., Drazen, J.C., Choy, C.A., Johnson, M.W., 2013. Methylmercury production below the mixed layer in the North Pacific Ocean. Nat. Geosci. 6 (10), 879–884.
Bosch, A.C., O'Neill, B., Sigge, G.O., Kerwath, S.E., Hoffman, L.C., 2016. Heavy metals in marine fish meat and consumer health: a review. J. Sci. Food Agric. 96 (1), 32–48.
Bower, J.R., Miyahara, K., 2005. The diamond squid (Thysanoteuthis rhombus): a review of the fishery and recent research in Japan. Fish. Res. 73 (1–2), 1–11.
Bowman, K.L., Hammerschmidt, C.R., Lamborg, C.H., Swarr, G., 2015. Mercury in the North Atlantic Ocean: the US GEOTRACES zonal and meridional sections. Deep-Sea Res. II Top. Stud. Oceanogr. 116, 251–261.
Bowman, K.L., Lamborg, C.H., Agather, A.M., 2020. A global perspective on mercury cycling in the ocean. Sci. Total Environ. 710, 136166.
Bustamante, P., Lahaye, V., Durnez, C., Churlaud, C., Caurant, F., 2006. Total and organic Hg concentrations in cephalopods from the North Eastern Atlantic waters: influence of geographical origin and feeding ecology. Sci. Total Environ. 368 (2–3), 585–596.
Cardoso, C., Lourenço, H., Afonso, C., Nunes, M.L., 2012. Risk assessment of methyl-mercury intake through cephalopods consumption in Portugal. Food Addit. Contam. Part A 29 (1), 94–103.
Carr, M.K., Jardine, T.D., Doig, L.E., Jones, P.D., Bharadwaj, L., Tendler, B., Lindenschmidt, K.E., 2017. Stable sulfur isotopes identify habitat-specific foraging and mercury exposure in a highly mobile fish community. Sci. Total Environ. 586, 338–346.
Chételat, J., Ackerman, J.T., Eagles-Smith, C.A., Hebert, C.E., 2020. Methylmercury exposure in wildlife: a review of the ecological and physiological processes affecting contaminant concentrations and their interpretation. Sci. Total Environ. 711, 135117.
Choy, C.A., Popp, B.N., Kaneko, J.J., Drazen, J.C., 2009. The influence of depth on mercury levels in pelagic fishes and their prey. Proc. Natl. Acad. Sci. 106 (33), 13865–13869.
Clarke, M.R., 1996. Cephalopods as prey. III. Cetaceans. Philos. Trans. R. Soc. Lond. B Biol. Sci. 351 (1343), 1053–1065.
Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, OJ L 364, 20.12.2006, p. 5–24. http://data.europa.eu/eli/reg/2006/1881/oj.
Connolly, R.M., Guest, M.A., Melville, A.J., Oakes, J.M., 2004. Sulfur stable isotopes separate producers in marine food-web analysis. Oecologia 138 (2), 161–167.
de Almeida Rodrigues, P., Ferrari, R.G., dos Santos, L.N., Junior, C.A.C., 2019. Mercury in aquatic fauna contamination: a systematic review on its dynamics and potential health risks. J. Environ. Sci. 84, 205–218.
Depew, D.C., Basu, N., Burgess, N.M., Campbell, L.M., Devlin, E.W., Drevnick, P.E., Wiener, J.G., 2012. Toxicity of dietary methylmercury to fish: derivation of ecologically meaningful threshold concentrations. Environ. Toxicol. Chem. 31 (7), 1536–1547.

dos Santos, R.A., Haimovici, M., 2002. Cephalopods in the trophic relations off southern Brazil. Bull. Mar. Sci. 71 (2), 753–770.
Eisler, R., 1987. Mercury Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review (No. 10). Fish and Wildlife Service, US Department of the Interior.
Elliott, K.H., Elliott, J.E., 2016. Origin of sulfur in diet drives spatial and temporal mercury trends in seabird eggs from Pacific Canada 1968–2015. Environ. Sci. Technol. 50 (24), 13380–13386.
Escobar-Sánchez, O., Galván-Magaña, F., Rosíles-Martínez, R., 2011. Biomagnification of mercury and selenium in blue shark Prionace glauca from the Pacific Ocean off Mexico. Biol. Trace Elem. Res. 144 (1–3), 550–559.
Evers, D., 2018. The effects of methylmercury on wildlife: a comprehensive review and approach for interpretation. In: The Encyclopedia of the Anthropocene, 5, pp. 181–194.
Evers, D.C., Sunderland, E., 2019. Technical Information Report on Mercury Monitoring in Biota: Proposed Components Towards a Strategic Long-term Plan for Monitoring Mercury in Fish and Wildlife Globally. UN Environment Programme, Chemicals and Health Branch, Geneva, Switzerland.
Fernández-Álvarez, F.Á., Braid, H.E., Nigmatullin, C.M., Bolstad, K.S., Haimovici, M., Sánchez, P., Villanueva, R., 2020. Global biodiversity of the genus Ommastrephes (Ommastrephidae: Cephalopoda): an allopatric cryptic species complex. Zool. J. Linnean Soc. 190 (2), 460–482.
Fitzgerald, W.F., Lamborg, C.H., Hammerschmidt, C.R., 2007. Marine biogeochemical cycling of mercury. Chem. Rev. 107 (2), 641–662.
Food and Drug Administration, 2018, November 07. FDA fish advice: technical information. Retrieved July 15, 2019, from. https://www.epa.gov/fish-tech/epa-fda-fish-advice-technical-information.
Gill, G.A., Fitzgerald, W.F., 1988. Vertical mercury distributions in the oceans. Geochim. Cosmochim. Acta 52 (6), 1719–1728.
Góngora, E., Braune, B.M., Elliott, K.H., 2018. Nitrogen and sulfur isotopes predict variation in mercury levels in Arctic seabird prey. Mar. Pollut. Bull. 135, 907–914.
Herrera, A., Betancourt, L., Silva, M., Lamelas, P., Melo, A., 2011. Coastal fisheries of the Dominican Republic. In: Coastal Fisheries of Latin America and the Caribbean, 44, pp. 175–217.
Herrera-Moreno, A., 2005. Historical Synthesis of Biophysical Information of Samaná Region. Dominican Republic.
Jereb, P., Roper, C.F., 2010. Cephalopods of the world. An annotated and illustrated catalogue of cephalopod species known to date. In: Myopsid and Oegopsid Squids, Volume 2. FAO.
Judkins, H.L., Vecchione, M., Roper, C.F., 2009. Cephalopoda (Mollusca) of the Gulf of Mexico. In: Gulf of Mexico Origin, Waters and Biota. Biodiversity, Vol. 1.
Kazama, H., Yamaguchi, Y., Harada, Y., Kaneko, N., Mizushima, H., Tsuchiya, K., Tanaka, M., 2020. Mercury concentrations in the tissues of blue shark (Prionace glauca) from Sagami Bay and cephalopods from East China Sea. Environ. Pollut. 115192.
Kidd, K.A., Hesslein, R.H., Fudge, R.J.P., Hallard, K.A., 1995. The influence of trophic level as measured by δ 15 N on mercury concentrations in freshwater organisms. In: In Mercury As a Global Pollutant (pp. 1011–1015). Springer, Dordrecht.
Lamborg, C.H., Hammerschmidt, C.R., Bowman, K.L., Swarr, G.J., Munson, K.M., Ohnemus, D.C., Saito, M.A., 2014. A global ocean inventory of anthropogenic mercury based on water column measurements. Nature 512 (7512), 65–68.
Lamborg, C.H., Hammerschmidt, C.R., Bowman, K.L., 2016. An examination of the role of particles in oceanic mercury cycling. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 374 (2081), 20150297.
Lavoie, R.A., Jardine, T.D., Chumchal, M.M., Kidd, K.A., Campbell, L.M., 2013. Biomagnification of mercury in aquatic food webs: a worldwide meta-analysis. Environ. Sci. Technol. 47 (23), 13385–13394.
Le Croizier, G., Lorrain, A., Sonke, J.E., Hoyos-Padilla, E.M., Galván-Magaña, F., Santana-Morales, O., Block, B., 2020. The twilight zone as a major foraging habitat and mercury source for the great white shark. Environ. Sci. Technol. 54 (24), 15872–15882.
Lipiński, M.R., Linkowski, T.B., 1988. Food of the squid Ommastrephes bartramii (Lesueur, 1821) from the south-west Atlantic Ocean. S. Afr. J. Mar. Sci. 6 (1), 43–46.
Lischka, A., Lacoue-Labarthe, T., Hoving, H.J.T., Javidpour, J., Pannell, J.L., Merten, V., Bustamante, P., 2018. High cadmium and mercury concentrations in the tissues of the orange-back flying squid, Sthenoteuthis pteropus, from the tropical Eastern Atlantic. Ecotoxicol. Environ. Saf. 163, 323–330.
Liu, G., Cai, Y., O'Driscoll, N. (Eds.), 2011. Environmental Chemistry and Toxicology of Mercury. John Wiley & Sons.
Liu, G., Cai, Y., O'Driscoll, N., Feng, X., Jiang, G., 2012. Overview of mercury in the environment. In: Environmental Chemistry and Toxicology of Mercury, pp. 1–12.
Lourenço, H.M., Anacleto, P., Afonso, C., Ferraria, V., Martins, M.F., Carvalho, M.L., Nunes, M.L., 2009. Elemental composition of cephalopods from Portuguese continental waters. Food Chem. 113 (4), 1146–1153.
Mason, R.P., Hammerschmidt, C.R., Lamborg, C.H., Bowman, K.L., Swarr, G.J., Shelley, R.U., 2017. The air-sea exchange of mercury in the low latitude Pacific and Atlantic Oceans. Deep-Sea Res. I Oceanogr. Res. Pap. 122, 17–28.
McCutchan Jr., J.H., Lewis Jr., W.M., Kendall, C., McGrath, C.C., 2003. Variation in trophic shift for stable isotope ratios of carbon, nitrogen, and sulfur. Oikos 102 (2), 378–390.
Minet, A., Manceau, A., Valada-Mennuni, A., Brault-Favrou, M., Churlaud, C., Fort, J., Lacoue-Labarthe, T., 2021. Mercury in the tissues of five cephalopods species: First data on the nervous system. Sci. Total Environ. 759, 143907.
Monteiro, L., Porteiro, F.M., Gonçalves, J.M., 1992. Inter-and intra-specific variation of mercury levels in muscle of cephalopods from the Azores. Arquipélago-Life Earth Sci. 10, 13–22.
Nho, E.Y., Khan, N., Choi, J.Y., Kim, J.S., Park, K.S., Kim, K.S., 2016. Determination of toxic metals in cephalopods from South Korea. Anal. Lett. 49 (10), 1578–1588.
Outridge, P.M., Mason, R.P., Wang, F., Guerrero, S., Heimburger-Boavida, L.E., 2018. Updated global and oceanic mercury budgets for the United Nations Global Mercury Assessment 2018. Environ. Sci. Technol. 52 (20), 11466–11477.
Overholtz, W.J., Link, J.S., Suslowicz, L.E., 2000. Consumption of important pelagic fish and squid by predatory fish in the northeastern USA shelf ecosystem with some fishery comparisons. ICES J. Mar. Sci. 57 (4), 1147–1159.
Pau, C., 2018. La pêche aux chipilouas (*Thysanoteuthis rhombus*) en Martinique: rapport technique (Rapport final du projet du CRPMEM de Martinique).
Penicaud, V., Lacoue-Labarthe, T., Bustamante, P., 2017. Metal bioaccumulation and detoxification processes in cephalopods: a review. Environ. Res. 155, 123–133.
Peterson, S.H., Ackerman, J.T., Costa, D.P., 2015. Marine foraging ecology influences mercury bioaccumulation in deep-diving northern elephant seals. Proc. R. Soc. B Biol. Sci. 282 (1810), 20150710.
Pethybridge, H., Daley, R., Virtue, P., Butler, E.C.V., Cossa, D., Nichols, P.D., 2010. Lipid and mercury profiles of 61 mid-trophic species collected off south-eastern Australia. Mar. Freshw. Res. 61 (10), 1092–1108.
Pinzone, M., Budzinski, H., Tasciotti, A., Ody, D., Lepoint, G., Schnitzler, J., Das, K., 2015. POPs in free-ranging pilot whales, sperm whales and fin whales from the Mediterranean Sea: influence of biological and ecological factors. Environ. Res. 142, 185–196.
Pinzone, M., Damseaux, F., Michel, L.N., Das, K., 2019. Stable isotope ratios of carbon, nitrogen and sulphur and mercury concentrations as descriptors of trophic ecology and contamination sources of Mediterranean whales. Chemosphere 237, 124448.
Post, D.M., 2002. Using stable isotopes to estimate trophic position: models, methods, and assumptions. Ecology 83 (3), 703–718.
R Core Team, 2018. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/.
Raimundo, Joana, Vale, Carlos, Canário, João, Branco, Vasco, Moura, Isabel, 2010. Relations between mercury, methyl-mercury and selenium in tissues of Octopus vulgaris from the Portuguese Coast. Environ. Pollut. 158 (6), 2094–2100.
Raimundo, J., Pereira, P., Vale, C., Canário, J., Gaspar, M., 2014. Relations between total mercury, methylmercury and selenium in five tissues of Sepia officinalis captured in the south Portuguese coast. Chemosphere 108, 190–196.
Rodhouse, P.G., 2005. C2. WORLD SQUID RESOURCES. Review of the State of World Marine Fishery Resources, p. 175.
Rodhouse, P. G., Pierce, G. J., Nichols, O. C., Sauer, W. H., Arkhipkin, A. I., Laptikhovsky, V. V., … & Sadayasu, K. (2014). Environmental effects on cephalopod population dynamics: implications for management of fisheries. In Advances in Marine Biology (Vol. 67, pp. 99–233). Academic Press.
Roper, C.F., Sweeney, M.J., Nauen, C.E., 1984. FAO Species Catalogue: Vol. 3. Cephalopods of the World. An Annotated and Illustrated Catalogue of Species of Interest to Fisheries. FAO Fisheries Synopsis, 3.
Schuhmacher, M., Batiste, J., Bosque, M.A., Domingo, J.L., Corbella, J., 1994. Mercury concentrations in marine species from the coastal area of Tarragona Province, Spain. Dietary intake of mercury through fish and seafood consumption. Sci. Total Environ. 156 (3), 269–273.
Seco, J., Xavier, J.C., Brierley, A.S., Bustamante, P., Coelho, J.P., Gregory, S., Tarling, G. A., 2020. Mercury levels in Southern Ocean squid: variability over the last decade. Chemosphere 239, 124785.
Shalini, R., Jeyasekaran, G., Shakila, R.J., Arisekar, U., Sundhar, S., Jawahar, P., HemaMalini, A., 2020. Concentrations of trace elements in the organs of commercially exploited crustaceans and cephalopods caught in the waters of Thoothukudi, South India. Mar. Pollut. Bull. 154, 111045.
Smale, M.J., 1996. Cephalopods as prey. IV. Fishes. Philos. Trans. R. Soc. Lond. B Biol. Sci. 351 (1343), 1067–1081.
Storelli, M.M., Marcotrigiano, G.O., 1999. Cadmium and total mercury in some cephalopods from the South Adriatic Sea (Italy). Food Addit. Contam. 16 (6), 261–265.
Storelli, M.M., Giacominelli-Stuffler, R., Storelli, A., Marcotrigiano, G.O., 2006. Cadmium and mercury in cephalopod molluscs: estimated weekly intake. Food Addit. Contam. 23 (1), 25–30.
Sun, Ruoyu, Jingjing Yuan, Jeroen E. Sonke, Yanxu Zhang, Tong Zhang, Wang Zheng, Shun Chen et al. "Methylmercury produced in upper oceans accumulates in deep Mariana Trench fauna." Nature Communications 11, no. 1 (2020): 1–9.
Tada, Y., Marumoto, K., Takeuchi, A., 2020. Nitrospina-like bacteria are potential mercury methylators in the mesopelagic zone in the East China Sea. Front. Microbiol. 11, 1369.
UN Environment, 2019. Global Mercury Assessment 2018. UN Environment Programme, Chemicals and Health Branch Geneva, Switzerland.
UNEP, 2013. Global Mercury Assessment 2013: Sources, Emissions. Releases and Environmental Transport, UNEP Chemicals Branch, Geneva, Switzerland.
Watanabe, H., Kubodera, T., Ichii, T., Kawahara, S., 2004. Feeding habits of neon flying squid Ommastrephes bartramii in the transitional region of the central North Pacific. Mar. Ecol. Prog. Ser. 266, 173–184.
Watanabe, N., Tayama, M., Inouye, M., Yasutake, A., 2012. Distribution and chemical form of mercury in commercial fish tissues. J. Toxicol. Sci. 37 (4), 853–861.
Weber, J.H., 1993. Review of possible paths for abiotic methylation of mercury (II) in the aquatic environment. Chemosphere 26 (11), 2063–2077.
Wiener, J.G., Krabbenhoft, D.P., Heinz, G.H., Scheuhammer, A.M., 2003. Ecotoxicology of mercury. In: Handbook of Ecotoxicology, 2, pp. 409–463.

Wolfe, M.F., Schwarzbach, S., Sulaiman, R.A., 1998. Effects of mercury on wildlife: a comprehensive review. Environ. Toxicol. Chem. 17 (2), 146–160.

World Health Organization. (2008). Safety Evaluation of Certain Food Additives and Contaminants (Vol. 68). World Health Organization.

World Health Organization, 2017, March 31. Mercury and health. Retrieved July 25, 2020, from. https://www.who.int/news-room/fact-sheets/detail/mercury-and-health.