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Inefficacy of cooking methods on mercury reduction from shark

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SUMMARY. Shark and other carnivorous fishes present high potential risk of excessive contamination by mercury. The distribution of mercury throughout the body of blue shark - *Prionace glauca* - was analysed, and the effects on mercury levels by frying and baking in a laboratory oven, and in a microwave oven, were measured. There was no significant statistical difference in mercury levels in the samples taken from regions near the head, or from central and tail parts, indicating homogeneous distribution of the metal in muscles throughout the body. Frying and baking did not affect original mercury levels present in blue shark. This study indicates that specific studies are needed to define the efficacy or inefficacy of the cooking methods on mercury reduction from fish, in order to clearly resolve divergent opinions in the literature.
Key words: Shark, fish, mercury, frying, baking, cooking.

RESUMEN. Ineficiencia de la fritura y el asado en la reducción de mercurio en tiburón. Los tiburones y otros peces carnívoros presentan alto potencial de riesgo por la excesiva contaminación con mercurio. La distribución de mercurio a través del cuerpo del tiburón azul - *Prionace glauca* - fue analisada, y medido los niveles de reducción de mercurio por el efecto de la fritura y el asado en horno de laboratorio y en horno de microondas. No hubo diferencias estadísticamente significativas en los niveles de mercurio en las muestras tomadas de la región próxima a la cabeza, región central y región próxima a la cola, indicando una distribución homogénea del metal en el músculo a través del cuerpo. La fritura y el asado no afectaron los niveles de mercurio presentes en el tiburón azul. Estudios específicos son necesarios para definir la eficiencia o ineficiencia de los métodos de fritura y asado en la reducción de mercurio del pescado, con el propósito de resolver definitivamente las opiniones divergentes de la literatura.
Palabras clave: Tiburón, pescado, mercurio, fritura, asado.

INTRODUCTION

Mercury occurs naturally in the Earth's crust, and can be highly biotoxic when its concentration in the environment and biota exceeds levels considered harmful for the ecosystem and consequently for human consumption (1).

Mercury can be found in the environment in several chemical forms with different toxicity potential. It can also be affected by microorganisms, through a process of methylation by which it becomes methylmercury, the chemical state that is most absorbed and accumulated by living organisms, especially in the aquatic biota. Methylmercury is the most toxic among mercury compounds (1,2).

The property of methylation induces biomagnification of mercury along the food chain, which means that the concentration at a given trophic level is elevated to the next highest. In consequence, animals that are found at the top of this food chain, such as carnivorous species of tuna, swordfish and shark - all present high potential risk of excessive contamination. Considering this characteristic, there is a high probability that toxic levels of mercury will reach humans through the fish (1,3).

Most published works on the presence of mercury in fish are based on concentrations *in natura* samples, there being little concern regarding domestic and/or industrial treatments that the fish undergo before consumption. Considering the relatively high temperatures used in the different methods of preparation, and the volatile characteristic of methylmercury, such treatments might sometimes reduce the concentration of this compound. This question has been explored in a number of laboratories around the world (4-12), but there is considerable divergence of opinions as to the true status.

In this article the distribution of mercury in blue shark was studied. Also studied were the effects upon original levels of mercury of frying and baking in a laboratory oven, and baking in a microwave oven.

MATERIALS AND METHODS

Preparation of the samples

Commercial samples of blue shark - *Prionace glauca*, decapitated, eviscerated, and without dorsal, ventral and caudal fins, weighing 45.3 ± 2.3kg and measuring 1.81 ± 0.20m, were obtained at the *Companhia de Entrepostos e Armazens Gerais* of the State of São Paulo (CEAGESP) in São Paulo, Brazil. In order to analyze the distribution of mercury in each animal, samples were comprised of three transverse slices, each collected from: (a) near the head, (b) the central area, and (c) the tail section. The samples were

ground, frozen (-25°C), and lyophilized, and the experimental half-slices were fried and baked. Frying was performed in an electric frying pan (Walita, Fritanella Plus model RI 6570) in commercial soybean oil, for 3.5 minutes, at 160±5°C. Baking was carried out in a laboratory oven (Fabbe-Primar model 219) for 45 minutes, at 170±5°C and in a microwave oven (National Jr. model) for 10 minutes at medium strength. At the end of each treatment, the internal temperature of the samples was immediately measured with a common thermometer. Internal temperatures of the samples at the end of frying, baking in laboratory oven and baking in microwave oven were 76.9±3.3°C, 87.9±3.7°C and 94.6±2.4°C, respectively. The experimental samples were ground, frozen (-25°C), and lyophilized following the experiments.

Analyses

The mercury in the lyophilized samples was measured in duplicate by atomic absorption spectrophotometer (13) as indicated in detail by Chicourel, Tenuta-Filho, Sakuma, Zenebon and Amorim (14). All the reagents were tested for the presence of mercury, and all glassware was decontaminated prior to the experiment by immersion for 48hrs in a 30% nitric acid solution and then rinsed with distilled deionized water.

The accurary and precision of the mercury analyses were validated by analysing "NBS Research Material 50 - albacore tuna" with a certified value of 0.95±0.10μg Hg/g (15). Then ten repetitions in duplicate were made and a mean value of 1.01±0.02μg Hg/g was found.

Results were analyzed statistically ($p<0.05$) by t-paired test and Kruskal-Wallis test (16).

RESULTS AND DISCUSSION

Distribution of mercury in blue shark

The tendency to accumulate excessive and dangerous concentrations of mercury in shark, such as the 4.9μg/g detected by Lyle (17) in *Sphyrna lewini*, or 4.7μg/g or 3.1μg/g detected by Morales-Aizpurúa, Tenuta-Filho, Sakuma and Zenebon (18) in *Sphyrna sp* and *Odontaspis sp*, respectively, make this marine animal a potentially toxic source of food. It should therefore only be consumed under toxicologically safe conditions.

Distribution of mercury in the shark was analyzed because of its importance under the aspects of monitoring, inspection, and control for consumption. Samples taken from three regions of the shark's body - near the head, the central region and near the tail - showed no discrepancy in mercury levels that could be considered statistically significant (Table 1). The results obtained therefore indicated homogeneous mercury distribution.

TABLE 1
Mercury (μg/g) distribution in blue shark's body (a)(b)

Samples	Near the head	Central region	Near the tail
1	0.61±0.04[a]	0.55±0.02[a]	0.59±0.04[a]
2	1.29±0.03[b]	1.27±0.08[b]	1.25±0.12[b]
3	1.67±0.22[c]	1.56±0.09[c]	1.65±0.06[c]

(a) Wet basis; (b) Mean ± standard deviation. Differences among the same sample indicated by the same superscript letters (a,b,c) were not statiscally significant ($p>0.05$).

In order to clarify whether sampling of different edible muscle tissues of the same fish could affect the results, Bortoli, Gerotto, Marchiori, Palonta and Troncon (19) published an interlaboratory study on 28 fishes. Bortoli, Gerotto, Marchiori, Muntau and Rehnert (20) also produced another study involving 6 predatory fishes. Among them the swordfish *Xiphias gladius* (3 specimens) and the sharks *Squallus acanthias* (2 specimens) and *Lamna nasus* (1 specimen) were analyzed. Such as the results in Table 1 the head, central and tail portions of the fishes showed no significant differences among themselves in mercury concentrations. Watling, Watling, Stanton, Macclurb and Engelbrecht (21) arrived at the same conclusion in relation to the shark *Isurus oxyrhinchus*. Mercury distribution studies in walleye indicated an even distribution throughout the fillet, thereby making it unnecessary to homogenize the entire fillet (12).

These results are important because they show that mercury levels can be analyzed in muscles from any region of the fish's body. Monitoring, inspection and control for consumption, mentioned above, are thus made easier, an important factor for large species. To quantify the mercury in blue shark *(Prionace glauca)*, Chicourel, Tenuta-Filho, Sakuma, Zenebon and Amorim (14) and Morales-Aizpurúa, Tenuta-Filho, Sakuma and Zenebon (18) took individual samples from the central region of the fish's body. About 30% of the samples bought commercially were unsuitable for human consumption (>1.0μg Hg/g), according to the brazilian legislation for predatory species (22).

Armbruster, Gutenmann and Lisk (9) considered that the distribution of mercury in the muscles of striped bass was homogenous when using one fillet as a control sample and analysing the effects of frying and baking on mercury. Other authors proceeded in a similar way with other species (6-8,12).

Effects of frying and baking on mercury in blue shark

Methylmercury is the compound that accounts for the highest presence of mercury in fish, and is sometimes the only form present (1). The possibility of reducing mercury

during frying and baking was studied, based on the volatility of methylmercury. For possible synergic effects NaCl and lemon juice were previously added to the sample.

The experiments performed, however, did not indicate that the original levels of mercury in blue shark had been reduced during frying in soybean oil, baking in the laboratory oven or baking in the microwave oven (Table 2).

TABLE 2
Mercury (μg/g) in raw and cooked blue shark (a)(b)

Cooking method	Samples	Raw shark	Cooked shark
Frying	1	7.22±0.22[a]	6.91±0.12[a]
	2	10.52±0.52[b]	10.05±0.48[b]
Baking in	3	3.18±0.16[c]	3.21±0.15[c]
laboratory oven	4	7.75±0.28[d]	8.18±0.18[d]
Baking in	5	3.36±0.11[e]	3.42±0.09[e]
microwave oven	6	8.50±0.41[f]	8.79±0.27[f]

(a) Dry basis; (b) Mean ± standard deviation. Differences among the same sample indicated by same superscript letters (a,b,c,d,e,f) were not statiscally significant ($p>0.05$).

As in the present experiment, some authors observed no reduction of mercury from frying or baking *Salmo gairdneri* (4), grouper, red snapper, Florida pompano and Spanish mackerel (8), striped bass (9), *Thunnus thynnus, Lamma nasus, Mustelus mustelus, Squalus fernandinus* and *Scyliorhinus canicula* (11) and walleye (12). No reduction of mercury was observed either when lemon juice was added to walleye fillets before frying (12).

The conditions indicated by the above authors [Table 3; except for Moretti, Marini and Bortoli (11), that do not mentioned the temperature and time used] were not exactly the same as those in the present experiment, and the original levels of mercury present in the samples varied greatly, from as little as 0.002μg Hg/g (8) to as much as 1.82μg Hg/g (4).

Armbruster, Gutenmann and Lisk (9) explained the results obtained as being due to methylmercury's chemical stability under the conditions for frying (80°C/10 minutes), baking in a common stove (80°C/31-40 minutes) and baking in a microwave oven (75-90°C/5-10 minutes) (Table 3). The conditions applied to frying blue shark (160±5°C/3.5 minutes), baking it in a laboratory oven (170±5°C/45 minutes) were apparently more favorable than those used by the majority of the authors (Table 3), for eventual removing methylmercury by volatilization.

TABLE 3
Frying and baking conditions that do not promoted mercury reduction

Cooking Methods	Temperature (°C)/ Frequency/Strength	Time (min)	Authors
Frying	177	1.8-4.3	Gall, Otwell and Koburger (8)
	80	10	Armbruster, Gutenmann and Lisk (9)
	177	8-12	Morgan, Berry and Graves (12)
	120-150	20	Limaverde-Filho, Campos, Goes and Pinto (23)
	160±5	3.5	Present paper
Baking in	177	9.4-24.3	Gall, Otwell and Koburger (8)
common oven	80	31-40	Armbruster, Gutenmann and Lisk (9)
	170	30	Pearce, Brooks and Reeves (4)
	115	10	Pearce, Brooks and Reeves (4)
	177	15-25	Morgan, Berry and Graves (12)
	170±5	45	Present paper
Baking in	2450MHz	0.8-1.8	Gall, Otwell and Koburger (8)
microwave oven	75-90	5-10	Armbruster, Gutenmann and Lisk (9)
	Medium strenght	10	Present paper

Contrary to the results shown in Table 2, Legrand and Le Moan (5), Anand (6), Lipre (7), Hernández García, Martínez Para and Masoud (10) and Limaverde-Filho, Campos, Goes and Pinto (23) obtained reduction of up to 65.5% of the mercury.

Legrand and LeMoan (5) reported reductions of 14% to 38% by frying rousette, containing 4.90-6.89μg Hg/g (dry basis). Frying at 170°C for 1-2 minutes, used by the above authors, did not differ much from frying the blue shark (160±5°C/3.5 minutes, Table 3), and do not apparently

explain the different results obtained.

Anand (6) obtained reductions of between 11.4% and 43.7% from frying for 4-7 minutes (temperature not mentioned) of fillets of *Pampus argentius*, originally containing 0.011 to 0.034μg Hg/g. The results of Lipre (7) were 26.5±2.4% and 17.6±6.2%, respectively, from frying and baking samples of fresh water species *Lucioperca lucioperca, Esox lucius, Perca fluviatilis,* and *Sprattus sprattus balticus*, originally containing < 2.5μg Hg/g. The above author, however, failed to indicate the temperature and time used.

Anand (6) and Lipre (7) considered the solubility (in oil) and the volatility of methylmercury as the causes for the reduction in mercury levels. As mentioned above, Armbruster, Gutenmann and Lisk (9), when justifying their results, indicated the contrary, namely, that mercury remained stable under frying (80°C/10 minutes, Table 3).

Hernández García, Martínez Para and Masoud (10) reported removal of mercury from several species of fish containing between 0.19 and 0.70μg Hg/g. The results were 23.7%, 31.6%, 41.5%, and 65.5%, respectively, from frying bonito, frying bonito followed by adding tomato, frying boqueron a la Milanese, and baking sardines. The authors suggested that the reduction in mercury was due to the temperature, the instability of the mercury when found in an environment containing organic acids from tomatoes, and dilution by the incorporation of other ingredients when fish was fried a la Milanese. The higher temperature was considered the cause in baking, due to the direct contact of the sample with the source of heat. The authors do not mentioned the temperatures and times used.

Limaverde-Filho, Campos, Goes and Pinto (23) studied the removal of mercury from fishes containing between 0.20 and 9.3μg/g (dry matter) by cooking at 120-150°C/20 minutes. Frying wasn't effective in the case of the "traíra" - *Hoplias malabaricus* (Table 3), but was effective for the "piraíba"- *Brachyplatystoma sp* - removing 12.9% of the mercury. In relation to "corvina"- Scianidae Family - and "piraíba" the cooking method used - "muqueca"- promoted a mercury reduction of 20 and 29.1%, respectively.

No specific factors were found that would justify the results described in Table 2 as compared to those reported by Legrand and Le Moan (5), Anand (6), Lipre (7) Hernández García, Martinéz Para and Masoud (10) and Limaverde-Filho, Campos, Goes and Pinto (23), who reduced mercury content between 11.4% and 65.5%. In general the absence of clearer descriptions which would allow reproduction of these experiments have made it difficult to come to more solid conclusions.

The results of the present paper and those from the literature indicate that further studies are needed. It is important to consider the variability of the mercury concentration in fish, the relation between inorganic mercury and methylmercury, and also the inside temperature effectively used. The true efficiency, or inefficiency, of methods of preparing fish in reducing mercury content prior to consumption must be more clearly defined, in view of the conflicting information found in the literature.

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