MERCURY CONTAMINATION IN PELAGIC FISHES OF THE GULF OF MEXICO

A Thesis

by

LIGITA KUKLYTE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2012

Major Subject: Marine Biology

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Approved by:

Chair of Committee,	Gilbert T Rowe
Committee Members,	Jaime Alvarado-Bremer
	Anja Schulze
	Thomas Shirley
Head of Department,	Gilbert T Rowe

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ABSTRACT

Mercury Contamination in Pelagic Fishes of the Gulf of Mexico. (August 2012)

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Chair of Advisory Committee: Dr. Gilbert T Rowe

Knowledge of mercury concentrations in fish is essential for human health protection. Mercury is a naturally occurring element that acts as a neurotoxin to humans and other species. The biologically available mercury form, methylmercury (MeHg), bio accumulates from small benthic invertebrates to large pelagic fish, and therefore high end consumers and terminal predators have elevated Hg concentrations. The main pathway of MeHg exposure in humans is by consumption of contaminated fish. In this study total Hg concentrations were measured in 10 Gulf of Mexico pelagic fish species using a DMA 80 analyzer. Total Hg concentrations ranged from 0.004 to 3.55 ppm (wet wt). The highest mean concentration (1.04 ppm, wet wt) recorded in king mackerel (*Scomberomorus cavalla*) exceeded FDA recommended criteria of 1ppm. Dolphinfish (*Coryphaena hippurus*) and vermilion snapper (*Rhomboplites aurorubens)* had lowest mean Hg concentrations (<0.3 ppm). The rest of the species were above the EPA advisory level of 0.3 ppm. Wahoo (*Acanthocybium solandri)*, greater amberjack (*Seriola dumerili*) and gag grouper (*Mysteroperca microlepsis*) had high Hg concentrations of

approximately 0.7 ppm wet wt. Blackfin tuna (*Thunnus atlanticus*) and yellowfin tuna (*Thunnus albacores)* had moderate Hg concentrations (0.39 and 0.36 ppm wet wt respectively). Little tunny (*Euthynnus alletteratus*) and blacktip shark (*Carcharhinus limbatus*) had mean concentrations of 0.69 and 0.51 ppm respectively. The relationship between fish length and Hg concentrations was significant for four species.

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CHAPTER I

INTRODUCTION

This chapter provides an overview of mercury (Hg) properties, sources in the environment and poisoning outbreaks. Hg transformation is reviewed in aquatic systems and bioaccumulation in food webs.

Mercury properties

Hg is a toxic, naturally occurring element, commonly known as quicksilver. Mercury, or any of its compounds, does not have a known biological metabolic function in organisms. Any amount of mercury is an indication for contamination (EPA 1985). Mercury is the only metal that is liquid at room temperature. It has a silver color with a metallic luster. Mercury exists in three oxidation forms: elemental (Hg^{o}), mercuric ion (Hg^{2+}) and mercurous ion (Hg_2^{2+}). Mercury can form organic and inorganic compounds. All three inorganic forms of Hg act similarly with regard to damaging cells at a molecular level, but mercuric form is the most toxic (Eisler 1987). Mercury freezes at -39^{o} C and has a boiling temperature of 357^{o}C. Mercury forms two salts from the mercuric oxide (Hg_2O) red powder and most reactive (HgO) orange- yellow powder. If heated to 630^{o}C it decomposes to oxygen and Hg. The two most important Hg salts are compounds with chlorine: mercurous chloride and mercuric chloride.

Mercury also forms salts with bromide, iodine, nitrates, sulfates, phosphates,

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This thesis follows the style of Marine Ecology Progress Series.

ammonium (Anon 1948). Chemically complex Hg compounds can form in solution under natural conditions and these are the most toxic to wildlife. Under low pH, redox environment and elevated temperatures Hg can be methylated by chemical or biological activities (Anon 1948). MeHg is the main form of Hg in fish, it makes up about 99% of total Hg concentration in fish muscle (Grieb et al. 1990).

Natural and anthropogenic mercury sources

The largest source of natural mercury is degassing directly from the earth's crust (Table 1). Hg is emitted into the atmosphere from oceans and other natural waters surfaces. Terrestrial sources of Hg include emissions from rocks, soils and vegetation. On land, vegetation uptakes elemental Hg from soil by roots and release Hg gas from the leaves. The Carson River Drainage Basin in Nevada is a historical gold mining site that is heavily contaminated by Hg. Plants growing there emit an additional 0.5 mg of Hg /m^2 to natural soil emissions (Leonard et al. 1998). Geothermal activity, volcanoes and natural forest fires also release Hg to the atmosphere. The total contribution to the atmosphere from natural sources adds up to about 5200 Mg of Hg yr^{-1} (Pirrone & Mason 2009). A part of naturally emitted Hg is previously produced anthropogenic Hg.

Humans contribute another 2909 Mg yr^{-1} of Hg to the atmosphere (Table 1) mainly by fossil fuel burning, especially coal. The atmospheric Hg concentration has increased between 3 to 20 fold since pre-industrial levels (Fain et al. 2009). In 1995 about 75% of total anthropogenic Hg entered the atmosphere from fossil fuel combustion (Pacyna & Pacyna 2002).

Table 1 Atmospheric annual Hg sources (Mg Hg yr^{-1}): natural and anthropogenic (Pirrone & Mason 2009).

Natural sources	Mg Hg yr^{-1}
Oceans and lakes	2682 and 96
Terrestrial vegetation, rocks and soils	1462
Biomass burning	675
Geothermal activity and volcanoes	90
Evasion after hg depletion event	200
Total natural sources	5207
Anthropogenic sources	**Mg Hg yr^{-1}**
Fossil fueled fired power plants	1422
Artisanal gold mining	400
Non ferrous metal manufacturing	353
Cement production	236
Caustic soda production	163
Waste disposal	187
Other	148
Total anthropogenic sources	2909
Total natural + anthropogenic sources	8116

Fossil fuel burning is still the largest contributor of human introduced atmospheric Hg, especially high emissions are from developing countries such as China and India due to high (and rising) coal consumption (Pirrone & Mason 2009). In addition, several other activities release Hg to the atmosphere such as gold mining, wood pulp industries, paint and cement production (Eisler 2006, Pacyna et al. 2006). In the year 2000 Europe and North America contributed 20% of global anthropogenic Hg emissions, whereas for Asian countries and Africa is was about 70% (Pacyna et al. 2006).

An estimated 334.17 billion metric tons of Hg exist in various global reservoirs (Eisler 1987). Majority resides in oceanic sediment (98% of the total) where it has a residence time of about 1 million years. Oceanic water contains another 1.24% of total Hg and has a residence time of about 2000 years. Nearly 850 metric tons of Hg is cycled in the atmosphere. Atmospheric Hg is easily transported and has a short residence time resulting to truly global distribution. Another 7 metric tons of Hg resides in biota (Eisler 1987).

Mercury cycle

In the atmosphere mercury circulates for about a year (Figure 1), oxidizes to the more reactive divalent form (Hg^{2+}) and subsequently is returned to the earth's surface by dry or wet deposition (Schroeder & Munthe 1998). Gaseous Hg can be transported long distances from point sources, making it a global pollutant. Mercury vapor is relatively inactive, but it is of high concern due to its volatility. Concentrations of gaseous Hg are

relatively higher in the Northern Hemisphere because of higher emissions (Pirrone & Mason 2009). The background concentration of Hg is nearly constant over the hemispheres, on average about 1.6 ng m^{-3} (Lin & Pehkonen 1999).

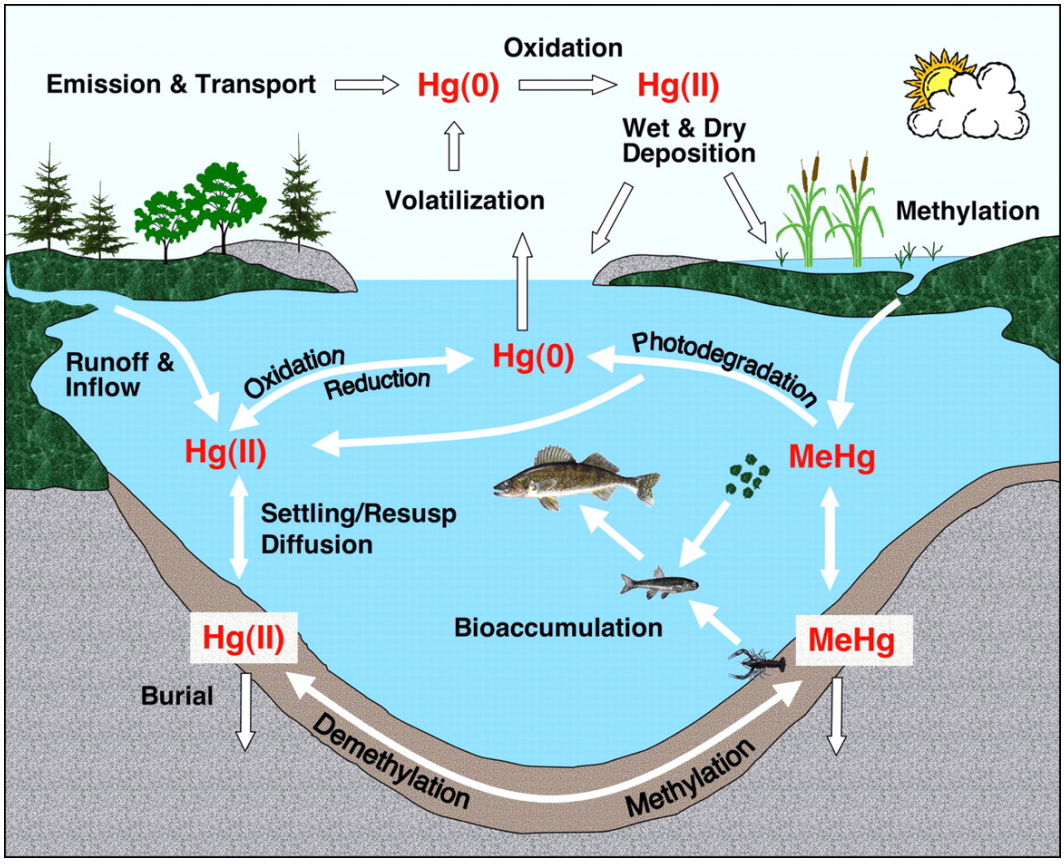

Figure 1 Mercury cycling and bioaccumulation in aquatic system (Engstrom 2007).

Elemental Hg can be oxidized by chemical reactions that depend on ozone, solar energy and water content in the atmosphere. Mercury oxidation is a photochemical

reaction that is highest at midday. Atmospheric Hg depletion events have been related to bromine release from sea ice in the arctic, with Br acting as a dominant oxidant (Obrist et al. 2011). Divalent and particulate Hg species are highly reactive forms of Hg, they are rapidly removed from atmosphere (days to weeks). These forms of Hg are referred to as reactive gaseous mercury (RGM). RGM are primarily dissolved in atmospheric waters or adsorbed to particulates in water droplets (Schroeder & Munthe 1998).

Mercury from the atmosphere can be deposited back to the earth's surface directly by adhesion to surfaces (Figure 1) (dry deposition) or deposited in rain (wet deposition) predominantly in the ionic form (Hg^{2+}) and as particulate Hg (Engstrom 2007). Once incorporated in soil, mercury can remain there for centuries as an organosulfur compound (Skyllberg et al. 2003). Mercury reduction and emission from soil is associated with physical factors such as temperature, pH, dissolved ions, solar radiation and moisture. At higher pH and temperature Hg mobilization and emission from soil increases (Gabriel & Williamson 2004).

Mercury is deposited into aquatic ecosystems by the same processes. In surface waters it occurs as dissolved free ions or forms complexes with the particulate matter (chloride, sulfide or dissolves organic matter). The concentrations between dissolved and particulate forms appear to be related to salinity. At low salinity in estuaries more Hg occurred in the dissolved form (79-87%) compared to the particulate fraction whereas at higher salinity in open water Hg forms complexes more readily (40-50%). Higher dissolved organic matter (DOM) concentrations may be associated with particulate Hg formation (Guentzel et al. 1996).

Bioaccumulation in food webs

Mercury concentrates in an organism through the process of bioaccumulation, a process in which a chemical pollutant is taken up through the diet (or absorbed by the respiratory surfaces) and its concentration increases within that organism as compared to the ambient environment (Arnot & Gobas 2006). Mercury bioaccumulates in aquatic food chains from algae, small benthic invertebrates to large pelagic fish and it reaches highest concentrations in the top trophic levels (Wang 2002). Hg concentrations in fish compared to the ambient water increases up to a factor of 10^6 (Engstrom 2007).

The inorganic Hg form is not retained in the organism after absorption through the intestinal wall and it is excreted at a rate similar to its uptake. In contrast, MeHg readily accumulates in an organism because of a slower excretion rate compared to uptake rate (Grieb et al. 1990). Elemental or inorganic divalent Hg can be converted to methylmercury (MeHg) by sulfate or iron reducing bacteria in aquatic sediments (Kelly et al. 2003). Microbial Hg methylation is enhanced under acidic, anoxic conditions and elevated temperatures (Merritt & Amirbahman 2009). This organic form of Hg is the toxic Hg species because it has a high potential to cross living cell membranes, form strong covalent bonds with proteins and rapidly bioaccumulate in aquatic food chains (Mason & Fitzgerald 1993). The source of the carbon methyl group is methylcobalamin that is synthesized by different strains of bacteria. The most common species responsible for Hg methylation is the sulfate reducing bacterium *Desulfovibrio desulfuricans* in anaerobic conditions in sulfur rich marine sediments (King et al. 2001). After exposure to heavy metals some plants can synthesize phytochelamin (PC) peptides, they bind to

heavy metals and are essential in the detoxification process in plants (Grill et al. 1985). Some fungi and worms also have PC mediated pathways for heavy metal detoxification. In animals, similar cellular mechanisms are possible, because phytochelatin synthase (mRNA) gene cloned into zebrafish embryos enhanced their tolerance to heavy metal toxicity (Konishi et al. 2006).

Nearly all Hg in fish is in a form of MeHg. Fish are able to absorb MeHg directly from water upon contact with their gills during respiration (Cember et al. 1978, Hall et al. 1997). In addition, MeHg can be produced in the gastrointestinal tract and on external surface layers (slime). Accumulation of MeHg directly through water was suggested to be as equally important as dietary exposure (Jernelöv & Lann 1971). Later experiments provided strong evidence that passive MeHg uptake through the gills is less significant (at most 15%) and the major pathway of Hg bioaccumulation in fish is through the diet (Hall et al. 1997).

Humans and other terminal predators are exposed to mercury through fish consumption (Pentreath 1976, Hall et al. 1997). Methylmercury is a neurotoxin that has been linked to cardiovascular problems in humans (Koren & Bend 2010). Although nutritious, some large pelagic fish species are contaminated with Hg and pose a great risk to consumers (Selin 2009). Pregnant women are especially vulnerable, because Hg easily crosses the placenta and reaches the fetus. Prenatal exposure may lead to lifelong adverse development (Kris-Etherton et al. 2002).

Poisoning outbreaks

One of the most severe and tragic mercury poisonings occurred in the1950s in the fishing village of Minamata Bay, Japan (Harada 1995). Especially affected were fishermen and their families. The source of Hg was untreated waste discharged to the bay from the factories that used inorganic Hg as a catalyst for acetaldehyde vinyl chloride production. The catalyst started to be used in 1932 and continued until 1971 (Eisler 2006). Overall, Minamata Bay received between 260-600 tons of Hg (Li et al. 2009). Sediments near the plant outfall had Hg concentrations of 2010 ppm, but concentrations decreased to 0.4–3.4 ppm with increasing distance from the bay. Inorganic Hg leached to the bay was diluted and diffused. Ultimately the Hg, was converted to organic methylmercury (MeHg) which entered the marine food chain. MeHg levels between 5.61 and 35.7 ppm were measured in fish and other marine products from the Minamata Bay (Harada 1995). People in the Japanese village consumed contaminated fish and shellfish, which induced severe Hg poisoning. The first recognition of symptoms occurred in 1956, but it was not linked to Hg until 1959 as a cause of disease. A total of 2,252 people exhibited severe physical, neurological, and mental symptoms and were eventually diagnosed with Hg poisoning or Minamata disease (Harada 1994). Of those diagnosed, 1043 have died and many cases were still unreported or pending (Kudo et al. 1998b). In adults, symptoms of Hg poisoning include tingling and numbness around the mouth, visual field constriction, mental disturbances, excessive salivation, slurred speech, difficulty walking, and tremors. These symptoms progress with time and are followed by loss of hearing, blindness and death (Risher et al.

2002). Children and pregnant women are particularly vulnerable because Hg is passed to the fetus through the placenta resulting in birth defects such as cerebral palsy, seizures, mental retardation and limb deformation (Harada 1978). Some bacteria are able to volatilize Hg in a series of enzymatic steps and naturally detoxify the environment. First, organic mercurial lyase breaks the carbon Hg bond and then mercuric reductase reduces divalent Hg to its elemental form, releasing Hg gas to the environment (Pak & Bartha 1998).

In the Minamata case microbial detoxification processes were too slow (18 yrs to detoxify 90% of contamination); therefore artificial mitigation was performed in 1984. Sediments containing more than 25 ppm of Hg were dredged and moved to a special landfill, which was permanently capped with sheets of vinyl plastic (Kudo et al. 1998a). Another example of mass poisoning happened in Iraq in 1971, where wheat seeds were treated with alkyl Hg to resist fungal disease upon planting. These crops were mistakenly used for human consumption in the process of bread production. Almost 6,500 Iraqis were hospitalized; many endured severe neurological symptoms and 459 died (Foulke 1995).

The main objective of this study was to measure Hg contamination in targeted Gulf of Mexico fish. In addition, the relationship between Hg levels and fish size was determined and Hg variations in different fish species based on feeding and life history traits were explored.

CHAPTER II

METHODS

Fish samples were gathered with hook and line at docks and offshore in three Gulf of Mexico regions (Figure 2). The majority of samples were collected in Venice, LA, (n= 48) and Freeport, TX, (n= 38), with the remaining collected in Port Aransas, TX (n= 28).

Sample collection and preservation

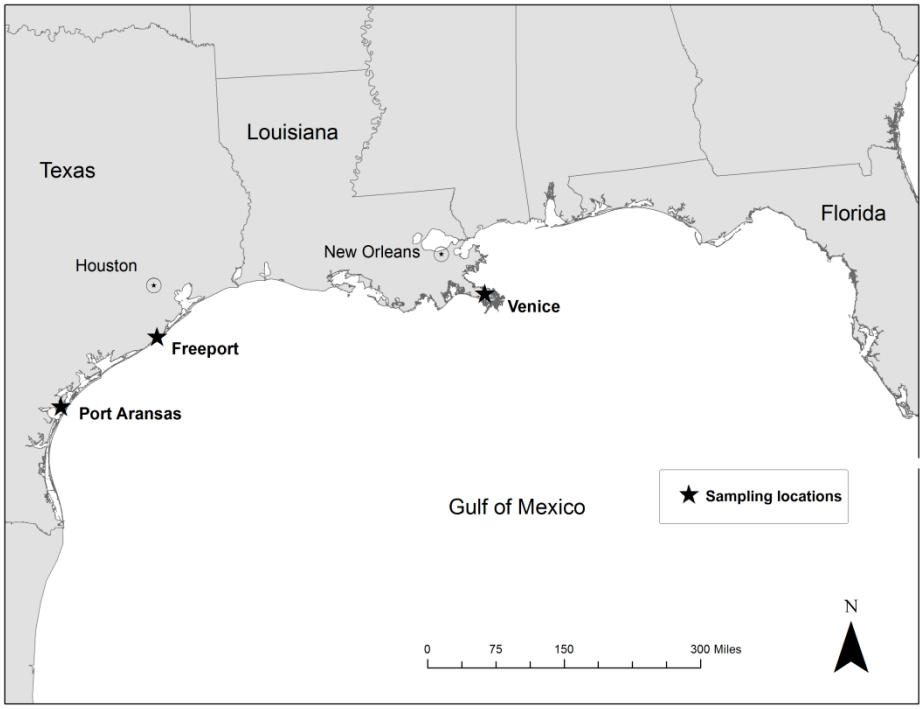

Figure 2 Map of sampling locations at the docks and offshore from Freeport and Port Aransas, Texas, and Venice, Louisiana, in the NW of Gulf of Mexico.

All the sampling was carried out from February to November in 2002. For each fish about 20g of muscle tissue was removed from the dorsal region behind the head, individually bagged, labeled and stored on ice for transportation to the laboratory where the samples were stored at -20°C until analyzed. Ten species were selected for this study (Table 2). These 10 were chosen because they are suspected to concentrate Hg, their life histories (age, growth rate and maximum sizes) are well established in the literature, their prey and their predators are known and they were available among the archived specimens at TAMUG.

Table 2 Common and scientific names and sample sizes of fish used in this study.

Common name	Scientific name	Sample size (n)
blackfin tuna (BX)	*Thunnus atlanticus*	11
yellowfin tuna (YT)	*Thunnus albacares*	11
little tunny (LT)	*Euthynnus alletteratus*	9
wahoo (WA)	*Acanthocybium solandri*	12
king mackerel (KM)	*Scomberomorus cavalla*	12
greater amberjack (AJ)	*Seriola dumerili*	12
gag grouper (GG)	*Mycteroperca microlepis*	10
vermilion Snapper (VS)	*Rhomboplites aurorubens*	11
dolphinfish (DF)	*Coryphaena hippurus*	12
blacktip shark (BS)	*Carcharhinus limbatus*	6
TOTAL	***10 species***	**106**

Mercury analysis

Fish white muscle tissues were analyzed for total Hg content using the direct Hg analyzer DMA-80, Milestone inc. Samples were taken from the freezer, cut into small (0.5-1 g) pieces and placed into 20 ml glass scintillation vials (purchased from Kimble). Vials were pre-cleaned by soaking overnight in 10% hydrochloric acid (HCl): subsequently they were combusted for 6 hours in the drying oven at 60°C. Vials with frozen fish tissues were placed into a vacuum freeze drier for 72 hours to ensure complete dehydration. Dry samples were homogenized and pulverized using a glass mortar and pestle. All utensils were cleaned with methanol to avoid cross contamination between samples. DMA-80 method is reagentless because it does not require multiple sample preparation steps (i.e. chemical digestion), instead, untreated samples are placed directly into the instrument. Pulverized samples were individually weighed (an accuracy of $\pm$ 0.001g) and placed into a nickel-coated sample boats for analysis. DMA 80 analysis starts with sample preparation, drying of the sample for moisture removal and mercury concentration. Drying times and temperatures were chosen based on the processes used by Cizdziel et al. (Cizdziel et al. 2002). The dried samples are then combusted to reduce all mercury species to the elemental form. Gold amalgamator is used for mercury sequestration. Subsequent amalgamator heating releases trapped mercury. Continuous stream of oxygen carries Hg gas through two cuvette cells and Hg is quantified using atomic absorption spectrometry. Mercury concentrations in the sample are calculated based on a most recent calibration curve. Daily calibration was performed following the EPA method 7473. Solid standard reference materials (SRM)

were used to generate quadratic calibration curve, where various weights of known mercury concentrations (in SRM) were plotted against the absorbance. SRM were purchased from the National Research Council of Canada (dogfish liver) DOLT-4 [2.58+/-0.22 ppm]. Three replicates of the first three fish samples were analyzed after calibration. Once the relevant percent difference was within 10%, then samples were analyzed in singles or repeated. Blanks (empty boats) were analyzed every eight samples to ensure that Hg was not carried over between samples. A separate SRM (fish protein) DORM-3 [Hg: 0.382+/-0.06 ppm] was analyzed every eighth sample to assure accuracy. Best fit calibration curves were obtained using a quadratic function with an average of R^2= 1.00 (ranged from 0.99- 1.00). Recovery of the SRM DORM-3 ranged from 99% to 115%, mean = 107% (table 3). The sample precision based on the coefficients of variation of the three replicates was 0.01-9.6 %, with a mean of 3.2%. Total Hg was used as a proxy for organic MeHg as it is well-established that > 95% of total Hg in edible muscle is MeHg (Bloom 1998). The DMA-80 has a detection limit of 0.01 ng Hg and a working range of 0.05-600 ng (EPA 2007). Recovery was calculated based on the mean published certified DORM -3 value, all recovered Hg in fish standard was within certified Hg range of 0.382- 0.44 ppm.

Statistical analyses

To explore the relationship between mercury concentration and fish size, a regression analysis was performed setting size as the independent variable and mercury concentration as the dependent variable (Table 2). A regression model is fitted such that

$$\log_{10} \text{ppm} = \beta_0 j + \beta_1 j * \text{cm}, \text{ for } j = 1, 2, \ldots, 10 .$$

using separate slopes (β_1) and intercepts (β_0) for each species. The use of $\log_{10}$ [Hg] ppm was chosen instead of [Hg] ppm as the dependent variable to get a better agreement with regression assumptions (normality of residuals, homoscedasticity). Assumptions of normality were examined using Shapiro Wilk test. To account for multiple comparisons the slopes in the above model were judged significant if a 99% confidence interval did not contain 0.

To examine regional and seasonal variation of Hg in fish marginal ANOVA was used setting location and species as main factor and Hg concentration as dependent variable. A significance level α=0.05 was used in all analysis. All calculations were performed using R version 2.13.1 (2011-07-08).

Table 3 Recovery accuracy of total Hg concentration in SRM DORM-3(fish tissue) [Hg: 0.382+/-0.06 ppm] as measured by DMA-80 during this study.

Total Hg [ppm] dry weight in DORM-3	
Determined	**% Recovered**
0.39	99.01
0.44	115.26
0.40	105.1
0.39	103.17
0.41	106.31
0.43	115.21
0.38	101.49
0.41	109.95
0.41	107.23
0.40	105.42
0.42	111.34
0.39	104.71
0.41	106.81
0.41	107.98
0.40	106.15
0.41	108.61
Average	**107.11**
SD	**4.47**

CHAPTER III

RESULTS

Mercury concentrations

Mercury concentrations of 10 commonly consumed pelagic Gulf of Mexico fish species are summarized and compared to national action levels and guidelines (Table 4). The highest Hg concentration in dry weight was recorded for a specimen of wahoo: 12.11 ppm, and the lowest in a specimen of yellowfin tuna: 0.035 ppm. To ease comparisons, all Hg concentrations were converted from dry to wet weight using the conversion equation

$$y = 3.80x + 0.04$$

where y = mean [Hg] ppm dry weight and x= mean [Hg] ppm wet weight (Cai et al. 2007). Mean Hg levels per species ranged between 0.05 and 1.04 ppm wet wt. The only two species that had concentrations below the 2002 US Environmental Protection Agency (EPA) reference dose of 0.3 ppm wet wt. were vermillion snapper and dolphinfish: 0.05 ppm and 0.21 ppm, respectively (EPA 2002). The rest of the examined species had higher Hg concentrations than the recommended advisory level set by the US EPA (Table 4). Wahoo, greater amberjack, and gag grouper and little tunny had similar mean Hg concentrations of approximately 0.7 ppm. Blackfin tuna and yellowfin tuna had mean Hg concentrations of 0.39 ppm and 0.36 ppm, respectively. King mackerel had the highest mean Hg concentration of 1.04 ppm wet wt., exceeding both

the EPA limit and the higher action level of 1.0ppm wet wt. set by the Food and Drug Administration (FDA 2001).

Table 4 Range and mean Hg concentration [ppm] in dry weight as measured with DMA 80. Converted mean Hg [ppm] to wet weight ±standard deviation of the mean. Mean length of species and range in cm.

Common name	Range of Hg [ppm] dry wt	Mean Hg [ppm] dry wt	Mean Hg [ppm] wet wt ±St dev	Mean size in (cm)	Size range in (cm)
*blackfin tuna	0.036-3.58	1.53	0.39±0.37	57	27-80
*yellowfin tuna	0.035-4.26	1.41	0.36±0.35	102	22-147
*little tunny	1.57-3.66	2.66	0.69±0.20	57	53-60
*wahoo	0.38-12.11	2.80	0.73±0.99	114	91-152
**king mackerel	2.04-5.92	3.99	1.04±0.3	82	70-98
*greater amberjack	1.8–5.76	2.85	0.73 ±0.27	88	73-119
*gag grouper	1.34-5.23	2.72	0.70±0.30	87	74-109
vermilion snapper	0.1-0.47	0.24	0.05±0.03	34	25-48
dolphinfish	0.07-4.33	0.86	0.21±0.37	67	43-123
*blacktip shark	0.48-5.94	1.99	0.51±0.54	95	56-173

*Above U.S. EPA 2002 recommended criteria level 0.3 mg Hg·kg wet wt^{-1}.
**Above FDA 2001 recommended criteria level 1.0 mg Hg kg wet wt^{-1}.
Conversion from dry to wet weight y = 3.80x + 0.04 were based on (Cai et al. 2007)

Relationship of Hg concentration and fish length

Regression analyses were defined to examine how Hg concentration in each fish species was related to length. Mercury concentrations were log transformed to meet the assumptions of normality and homoscedasticity. Positive trends were detected for all species. Four species in this study had a significant positive relationship between Hg concentration and fish length namely, blackfin tuna, yellowfin tuna, wahoo and dolphinfish (Table 5). The regression model was significant ($F_{19, 86} = 37.31$, $p < 10^{-16}$) and the regression assumptions were met. No point was unduly influential as all Cook's distances were below 0.5. The 99% confidence intervals were calculated for the regression slopes for each species. For the slopes that were significantly above 0, the regression model for the Hg level in that species was calculated.

Table 5 Confidence intervals (99%) for regression slope and regression model for each species, along with the back transformed regression model.

Species name	99% confidence interval	Regression model	Transformed regression model
amberjack	(-0.008, 0.015)	ns	ns
blacktip shark	(-0.001, 0.0082)	ns	ns
dolphin fish	(0.133, 0.023)	$\log_{10}$ppm=-1.771+0.018∗cm	ppm = 0.0167*1.043cm
gag grouper	(-0.0034, 0.025)	ns	ns
little tunny	(-0.0537, 0.111)	ns	ns
vermillion snapper	(-0.0089, 0.03)	ns	ns
wahoo	(0.0107, 0.0282)	$\log_{10}$ppm=-2.0219+0.02∗cm	ppm = 0.0009*1.045cm
blackfin tuna	(0.019, 0.034)	$\log_{10}$ ppm= -1.762+0.027∗cm	ppm = 0.0173*1.064cm
king mackerel	(-0.011, 0.025)	ns	ns
yellowfin tuna	(0.009, 0.016)	$\log_{10}$ppm= -1.416+0.012∗cm	ppm = 0.0384*1.0288cm

The model for blackfin tuna had an increase in Hg levels of 6.41% for each additional cm in length (Figure 3). The rate of Hg accumulation was calculated to be lowest for yellowfin tuna, with a 2.87% increase of Hg concentration per cm of length (Figure 4). Models for wahoo and dolphinfish had a 4.51% and 4.3 % increase in Hg concentration per cm of length, respectively (Figures 5 and 6).

Mercury concentrations and location

Regional variations in Hg concentrations were found with ANOVA. Significant differences (p value < 0.001; sequential Bonferroni test) in Hg concentrations occurred between the three locations, however differences between locations and species could not be determined.

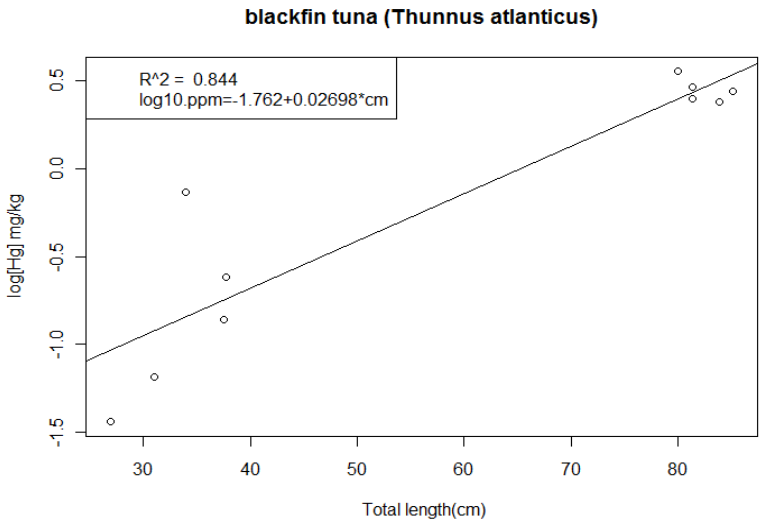

Figure 3 Mean Hg concentration log [Hg] ppm for blackfin tuna (*Thunnus atlanticus*) versus total length of fish (cm).

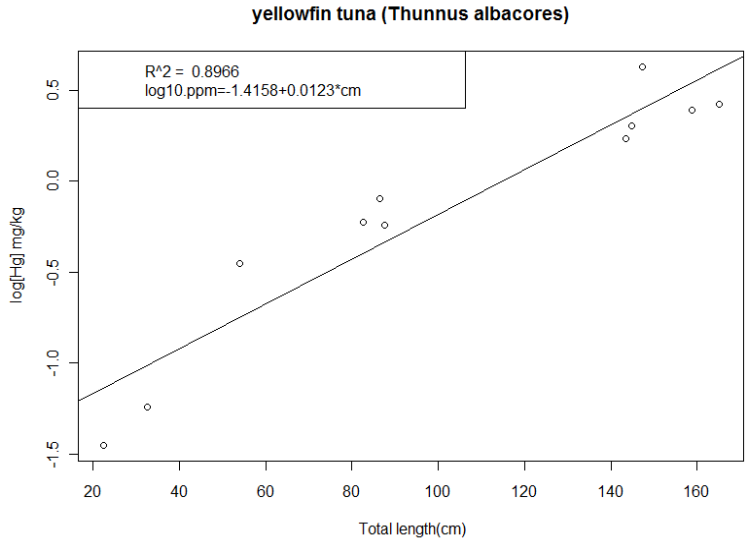

Figure 4 Mean Hg concentration log [Hg] ppm for yellowfin tuna (*Thunnus albacares*) versus total length of fish (cm).

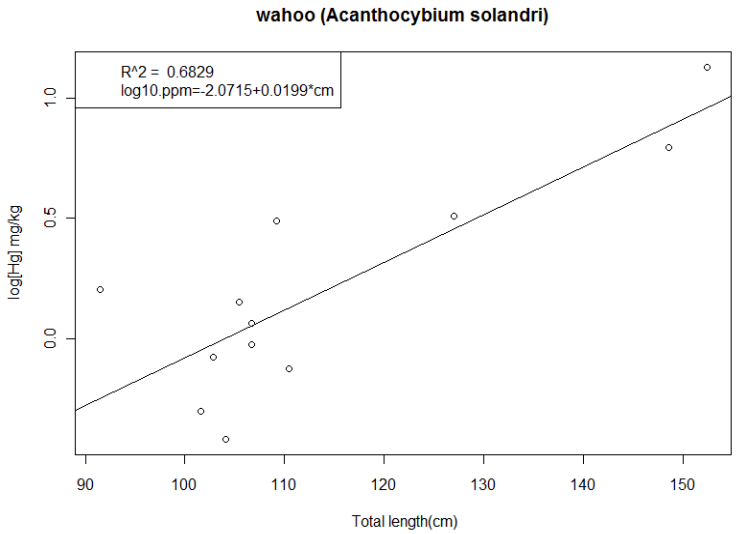

Figure 5 Mean Hg concentration log [Hg] ppm for wahoo (*Acanthocybium solandri)* versus total length of fish (cm).

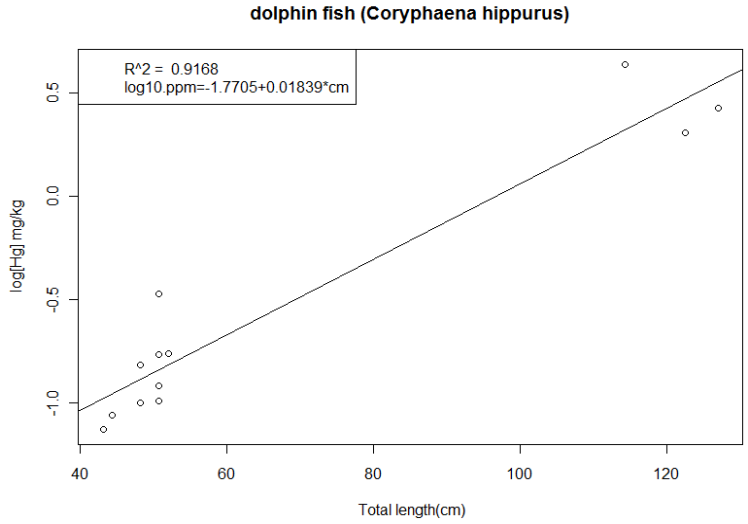

Figure 6 Mean Hg concentration log [Hg] ppm for dolphinfish (*Coryphaena hippurus*) versus total length of fish (cm).

CHAPTER IV

DISCUSSION

Mercury concentrations were variable within and between 10 pelagic Gulf of Mexico fish species examined in this study (Table 4). Mean Hg levels among species ranged between 0.05 and 1.04 ppm wet wt, such variation can be primarily explained by fish length, where larger fish had higher Hg concentrations. Large aquatic organisms tend to accumulate Hg possibly as a result of rapid uptake coupled with slow Hg elimination rates (Downs et al. 1998). In addition, as fish grow larger they generally consume larger prey that possibly have higher concentrations of mercury.

Compared to national action levels and guidelines (Table 4) only vermillion snapper (0.05 ppm) and dolphinfish (0.21 ppm) had mean Hg concentrations below the EPA reference dose of 0.3 ppm wet wt.; the rest of the examined species had higher Hg concentrations. Humans should eat no more than one meal per month of fish that have Hg concentrations of 0.5 ppm wet weight, where a meal is described as 226.8 g of uncooked edible fish tissue for a body weight of 70 kg and methylmercury reference dose of $1x\ 10^{-4}$ mg MeHg $kg^{-1}day^{-1}$ (EPA 2002). This advisory would apply for all species examined in this study except vermillion snapper and dolphinfish.

King mackerel had the highest mean Hg concentration (1.04 ppm wet wt.) exceeding both the EPA and the FDA limits, however it was not the largest fish in the study (Table 4). Other factors, related to life history traits, may cause variable mercury concentrations in fish.

Mercury concentration and life history traits

Mercury in fish has been linked to size, age and trophic position in prior research (Lange et al. 1994, Adams & McMichael 2007, Bank et al. 2007). To compare their relative importance for each species, life history variables are compared (Table 6).

Table 6 Life history traits from literature: trophic adult position (Pauly & Palomares 2005), lifespan (maximum age in years), maximum length (cm), length at year one (cm) and percentage (%) of bony fish in their diet.

Species name	Trophic adult position	Max age	Max length	Length at year one	Fish % in diet	References
blackfin tuna	4.13	5	93	45	70%	(Doray et al. 2004) (Robert et al. 2010)
yellowfin tuna	3.70	5.5	259	60	50%	(Davidoff 1963, Manooch et al. 1985)
little tunny	3.80	7	100	35	67%	(Johnson 1984)
wahoo	4.5	10	195	70	97%	(McBride et al. 2008)
king mackerel	4.5	20	151	55	76%	(Finucance et al. 1990, Vries et al. 1990)
greater amberjack	3.3	13	140	72	95%	(Manooch & Potts 1997)
gag grouper	3.0	13	120	27	50%	(Manooch & Haimovici 1978, Mullaney & Gale 1996)
vermilion snapper	2.9	10	58	19	38%	(Grimes 1978, 1979)
dolphinfish	3.0	4	152	72	95%	(Beardsley 1967)
blacktip shark	3.2	9	208	73	90%	(Branstetter 1987)

King mackerel had the highest mean Hg concentration, this can be tentatively linked to its long lifespan yielding longer exposure times for older fish. King mackerel occupies the highest trophic position in comparison to other species in this study. Like other predatory fish species king mackerel feeds mainly on fish (sardines, mullet, drums, jacks). The king mackerel diet even as a juvenile is that of a pelagic carnivore. Subsequently it can accumulate relatively high Hg levels (Naughton & Saloman 1981). Hg received with diet can explain most of the variation in Hg. This species is known to concentrate mercury and advisories at a state and regional level warn consumers of potential Hg risks (FDA 2001).

The Lowest Hg concentrations were recorded for vermillion snapper (0.05 ppm) which may be attributed to the small size of the fish. In addition, a low trophic position is inherently linked to the consumption of small prey and as such it can be expected that they have accumulated lesser quantities of Hg.

Given the large number of potential factors influencing Hg accumulation in fish, it was not surprising to see some trends that were at first counter-intuitive. The comparison of blackfin to yellowfin tuna is an interesting case. Blackfin tuna is a smaller sized tuna that is distributed in the Atlantic Ocean between 40°N to 25°S in latitude. Even though few individuals were reported to live to similar age of yellowfin tuna (5 years), it is very uncommon to get a blackfin tuna larger than 68 cm and older than 3 years (Doray et al. 2004).

Yellowfin tuna is a cosmopolitan pelagic species that inhabits tropical and subtropical waters of Atlantic and Pacific Oceans. Due to physiological and

morphological adaptations it can keep its core red muscles above ambient temperatures, thus enabling it to dive to deeper colder waters (Brill et al. 1999b). It is a large fish (~2 meters) that has a relatively short lifespan, with the oldest fish reaching about 5.5 years (Davidoff 1963). At small sizes both species had about the same Hg concentrations. However, at a larger size (80cm), blackfin tuna had slightly higher Hg concentrations than yellowfin tuna twice the size (160). This observation can be explained by their differing dietary exposures. Blackfin tuna and yellowfin tuna consume a variety of fish, crustaceans and mollusks (Manooch et al. 1985). Predominantly small fish species are the prey of blackfin tuna, whereas yellowfin tuna tend to feed on a combination of small fish and cephalopods such as squid. Interestingly, the Hg content in squid is typically of the order of 0.1 ppm, which is a lot lower than concentrations found in fish consumed by the tuna (Falandysz 1990). It is one of the largest species (maximum length 259 cm's) of the mackerel and tuna family (Scombridae). Both tuna species are highly migratory (swimming thousands of miles), but blackfin tuna are neritic and forage closer to the shoreline, generally over continental shelves. In contrast, yellowfin tuna are oceanic swims continuously in the top 100 meters of the water column and feeds opportunistically on available prey (Brill et al. 1999a). As a result both species may be exposed to a variety of different prey containing varying Hg concentrations (Adams et al. 2003). Because of these differing feeding scenarios, one can conclude that dietary exposure is a main pathway resulting in high Hg burdens in marine fish (Wang 2002). Trophic position and food habits lead to very different Hg concentrations even for sympatric or closely related species. Bank et al. (2007) documented an increased mean

Hg concentration in grey snapper (0.15 ppm) compared to that in red snapper (0.06 ppm). They related this to a slightly higher trophic level in combination with a preference for more pelagic bony fish rather than benthic prey.

Greater amberjack is a large pelagic species and is expected to have high Hg burdens because of its longevity (13 yrs), but in this study the mean age was about 3 years (87 cm) so higher Hg concentrations could be explained by the juvenile greater amberjack being active predators.

Vermillion snapper had the lowest Hg levels recorded (0.05 ppm); this fish was also the smallest from all fish examined growing to about 60 cm in length (Grimes 1978).

The low mean Hg concentration (0.21 ppm) in dolphinfish can be explained by their relatively short lifespan (3 - 4 years) and thus short Hg exposure time. Another reason for observed lower Hg burdens could be growth dilution. During very fast growth prior the maturation, the volume of the body increases realatively fast and a unit of the body weight has lower metabolic turnover and lower Hg concentration compared to adults that stop growing and thus accumulate more Hg.

Gag grouper is distributed in brackish and marine waters of western Atlantic Ocean in the upper 20 -100 meters. It is a schooling fish that lives in tropical waters and it prefers structurally complex habitat such as coral reefs and bottom sponges and estuaries with shallow grass beds during its earlier life stages. Its diet is less dependent on bony fish (Table 6). Gag grouper undergo ontogenic shifts in their diet as they grow; juveniles (15-25 mm) consume calanoid copepods, but as they grow they switch to

epibenthic predation at 20-30 mm: amphipods, copepods and decapods become more important in their diet) (Mullaney & Gale 1996). Our sample representative was primarily of older adults that rely on fish rather than juveniles who rely on a low Hg concentrated diet; this might explain higher Hg concentrations (0.70ppm).

Wahoo had the highest Hg concentration among targeted species - 11.2ppm dry weight (0.73 wet weight), exceeding the EPA advisory level. Wahoo is a highly mobile, globally distributed fish currently suggested to comprise just one population worldwide (Theisen et al. 2008). The species has high commercial and recreational fisheries importance. Fish accumulate Hg upon consumption of prey (Wang 2002). Wahoo is a piscivore that feed mainly on mackerel, butterfish, herring, scads and jacks. In general fish comprise about 97% of the diet of wahoo, but it also preys on invertebrates such as squid (Adams 2010). Wahoo can attain burst speeds and catch larger prey and they can section the prey with their sharp teeth. In addition wahoo grow rapidly, especially its first year, and can live up to ten years. In spite of a long potential longevity, most reported age averages less than two years, with a mean of 1.8 years (McBride et al. 2008). Feeding habits and rapid growth along with high metabolic requirement for pelagic lifestyle may result in high observed Hg concentrations in muscle.

There are two possible reasons why blacktip sharks have high Hg concentrations. First, they give birth live and have a slow growth rate; therefore they might accumulate more by the time they reach maturity compared to other fish that develop from an egg with a smaller mercury burden. In addition, sharks are top predators and their diet

include mostly fish (menhaden, croaker, mackerel) or other smaller elasmobranchs (skates and rays) (Castro 1996).

In general, the results and insights gained from this work confirm that species that are higher in the food chain, such as king mackerel, accumulated more Hg compared to vermillion snapper, a smaller species at a lower trophic level.

Mercury concentration and fish length

Positive linear relationships were found between total length and logarithmic Hg concentration in four fish species: yellowfin and blackfin tuna, wahoo and dolphinfish (Figures 3-6). Other species had a similar behavior: a positive slope was evident, but the relationship was not significant. A larger sample size (or range of sizes included in the samples) might have resulted in a significant relationship in these species. A significant relationship between total length and Hg concentration has been previously reported for king mackerel (Cai et al. 2007) and little tunny (Adams 2004).

The rate of Hg accumulation in blackfin tuna was found to be more than double that of yellowfin tuna: for every centimeter of growth the total Hg concentration is increased by 6.41% and 2.87%, respectively. The different dietary exposure of the blackfin tuna is likely the reason for such a fast rate of Hg accumulation. Blackfin tuna predominantly feed on prey having a higher Hg concentration and therefore their exposure is increased.

Wahoo also had a significant relationship between length and Hg concentration (Figure 5). It had a higher Hg increase rate (4.51) per cm of growth yellowfin tuna.

Wahoo occupies higher trophic level and the sample of wahoo was comprised of relatively large fish (mean of 114 cm).

Dolphinfish is oceanic fish, generally piscivorous and has a high metabolic demand (Oxenford & Hunte 1999) . The significant relationship between length and Hg concnetrations (4.3) is expected for fish with high trophic position and high metabolic demands.

This study was consistent with previous investigations reporting positive relationships between fish length and muscle tissue Hg concentration (Sonesten 2003, Trudel & Rasmussen 2006, Cai et al. 2007).

Mercury concentrations and location

Variations in Hg concentrations between species could be related to foraging location. Most of the species in this study are highly migratory and are capable of covering long distances during their lifetime (FAO 1994). Some of the species may only spend part of their time in the Gulf of Mexico; therefore it would be very difficult to relate their mercury concentrations to location.

Location and environmental variables (pH, temperature, POM) have all been linked to Hg accumulation in fish (Merritt & Amirbahman 2009). Significant regional differences in Hg concentration were observed for king mackerel in the Atlantic (0.94 ppm) and Gulf locations (1.51 ppm) (Adams & McMichael 2007). These differences appear to be related to diet, variable growth rates or differences in the mercury availability between two locations.

Significant differences exist between yellowfin tuna Hg concentrations of the Eastern Pacific (Baja California) (0.14) and the equatorial zone (0.21) (Ordiano et al. 2011). Equatorial species had higher levels of Hg because the fish were larger compared to those from Baja California Sur. In addition, there were significant differences detected between locations that could be related to higher methylation rates influenced by increased organic matter in more coastal areas.

CHAPTER V

CONCLUSIONS

Anthropogenic activities increase the natural background Hg levels and disrupt the biochemical Hg cycle. Once in the environment Hg undergoes transformation from a relatively inert to a highly toxic form. Through complicated biological and chemical processes the same Hg that was released by humans is recycled and is returned back to humans. Over long chronic Hg exposure, even at low tolerable levels, Hg leads to adverse health effects. Mercury is potential neurotoxin and has been linked to cardiovascular problems in humans (Mozaffarian & Rimm 2006). Consumption of marine fish accounts for the greatest MeHg exposure in United State population (Sunderland 2006).

Mercury concentrations in fish were variable across species and between the individuals of same species. In general larger, older fish that occupy higher trophic levels have higher Hg concentrations when compared to younger and smaller fish. The highest mean concentration 1.4 ppm (wet wt) recorded for king mackerel (*Scomberomorus cavalla*) exceeded FDA recommended criteria of 1ppm can be explained by high trophic level of this veracious predator.

In addition there are many different biological and environmental factors, such as diet, that influence MeHg burden in fish. Vermilion snapper *(Rhomboplites aurorubens)* had the lowest Hg concentrations (0.05ppm) due to the small size of the fish but also because its diet is composed of a smaller percentage of fish.

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