Collection Year, and Trophic level

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ABSTRACT

Total mercury (Hg) concentrations were determined in the tissues of 11 species of pelagic fishes, with a special emphasis on apex predators (large vertebrates). Highest mercury concentrations were observed in blue marlin (*Makaira nigricans*), Carcharhinid sharks (genus *Carcharhinus*)and little tunny (*Euthynnus alletteratus*), ranging from 1.0 to 10.6 ppm. Moderate to low concentration (< 1.0 ppm) were observed in greater amberjack (*Seriola dumerili*), blackfin tuna (*Thunnus atlanticus*), cobia (*Rachycentron canadum*), king mackerel (*Scomberomorus cavalla*), little tunny (*Euthynnus alletteratus*), wahoo (*Acanthocybium solandri*), yellowfin tuna (*Thunnus albacares*) and dolphinfish (*Coryphaena hippurus*). For the majority of species examined, contaminant loads of mercury did not vary significantly between two consecutive years (2002 and 2003) and between two adjacent locations (Texas and Louisiana). The relationship between Hg concentration and fish size was also explored in certain species. Several species showed a positive relationship between mercury level and body size. Natural dietary tracer, stable isotopes of nitrogen also showed that Hg levels in fish tissues were positively associated with trophic position. Our findings in this study not only added to the information on mercury contamination in pelagic fish, but also furthered our understanding on mercury accumulation in these fish.

KEY WORDS: Mercury concentration, pelagic fish, size, location, trophic position, Gulf of Mexico

Bioaccumulation de Mercurio en Peces Pelágicos del NO Golfo de México

Fueron determinadas las concentraciones de Metil Mercurio (MMHg) en los tejidos de 10 especies de peces pelágicos, con especial énfasis en predadores del ápice de la cadena trofica (grandes vertebrados). Altas concentraciones de Mercurio fueron observadas en billfish y en tiburones (e.s. blue marlin, maco shark), fluctuando de 1.0 a 19.6 ppm. Moderadas a bajas concentraciones (<1.0 ppm) fueron observadas en greater amberjack, blackfin tuna, cobia, king mackerel, little tunny, wahoo, yellowfin tuna y dolphinfish. Las cargas contaminantes de mercurio variaron en función del año y la localización

geográfica. Para la mayoria de las especies examinadas, fueron observadas significativamente altas concentraciones de MMHg en LA comparadas con TX. También, la mayoria de las especies examinadas, mostraron un incremento en la concentración de MMHg en 2003 comparado con 2002. Las relaciones entre la concentración de MMHg
Y el tamaño del pez fueron exploradas en ciertas especies. Algunas especies mostraron una relación positiva entre su nivel de MMHg y el tamaño del cuerpo, lo cual indica que la concentración de MMHg es también función del tamaño del cuerpo. Los trazadores naturales de dieta (isótopos estables, acidos grasos) encontrados en tejidos de consumidores, fueron conectados a concentraciones de MMHg, para posteriormente explorar procesos responsables de los elevados niveles en algunos consumidores. El análisis del isótopo estable de nitrógeno, indicó que los niveles de MMHg fueron positivamente asociados con la posición trófica del consumidor. Además, los perfiles de ácidos grasos (proxy para historia dietaria), fueron similares entre consumidores con elevado MMHg, sugiriendo que la acumulación de MMHg es directamente conectada con historia de la alimentación.

PALABRAS CLAVES: Metil Mercurio, bioaccumulation, peces pelágicos, Golfo de Mexico

INTRODUCTION

There are three forms of mercury in the natural environment (elemental, inorganic and organic) among which methylmercury, the organic form, is the most toxic (Fitzgerald 1991). Elemental mercury (Hg^0) is released into the environment by natural sources like volcano eruptions or by industrial production like gold mining. The Hg^0 vapor may be oxidized into divalent mercury (Hg^{2+}), which may be subjected to methylation by sediment microbiota. Methylmercury is then bioaccumulated in aquatic food webs (Malm et al. 1990). Methylmercury is a neurotoxin that can cause nervous system disorders, and fetuses and infants are more susceptible to brain damage from methylmercury since it inhibits cell division and migration (Clarkson 1987). The effects of localized methylmercury contamination in natural waters have been tragically demonstrated by mass poisonings at Minamata and Niigata, Japan. Because methylmercury comprises more than 80% of the total Hg in fish, often total mercury is measured to represent the methylmercury level in fish (Andersen and Depledge 1997). Fish are also the primary dietary source of methylmercury in humans (Clarkson 1992). Currently, fish consumption advisories for mercury exist in 44 states (U.S. EPA 2001, FDA 2001). Marine fish of greatest concern include sharks, swordfish, king mackerel, and tilefish, all of which are recreationally caught in waters of the Gulf of Mexico. A survey of mercury levels in finfish collected from the Gulf of Mexico was recently compiled by Ache et al. (2000), who found that 15 of the 26 species surveyed exceeded EPA (U.S. Environmental Protection Agency) consumption advisory level of 0.3 ppm mercury (U.S. EPA 2002).

We studied 11 species of pelagic fish that are commonly caught in the recreational fishery of northwestern Gulf of Mexico: blackfin tuna (*Thunnus* *atlanticus*), blue marlin (*Makaira nigricans*), cobia (*Rachycentron canadum*), dolphinfish (*Coryphaena hippurus*), greater amberjack (*Seriola dumerili*), king mackerel (*Scomberomorus cavalla*), little tunny (*Euthynnus alletteratus*), Carcharhinid sharks (genus *Carcharhinus*), swordfish(*Xiphias gladius*), wahoo (*Acanthocybium solandri*), and yellowfin tuna (*Thunnus albacares*). Because methylmercury in fishes is primarily transferred up the food chain, we examined nitrogen stable isotope as tracer of nutritional history since consumer tissues reflect the isotopic composition of prey in a predictable manner (Peterson and Fry 1987). Nitrogen stable isotope ratios ($d^{15}N$) in the muscle tissue of marine consumers are typically enriched by approximately 3 to 4 ‰ per trophic step and have been used to delineate the trophic positions of consumers (Owens 1987, Wada et al. 1991).

The objectives of this study were:

i) Measure mercury concentration in the tissue of pelagic fishes from the NW Gulf of Mexico,
ii) Examine spatial variation (Louisiana versus Texas) and annual (2002 versus 2003) variation in concentration of mercury in the tissue of pelagic fishes,
iii) Examine the relationship between fish size to mercury in pelagic fishes, and
iv) Examine the relationship between trophic position (based on analysis of stable nitrogen isotopes) and mercury in pelagic fishes.

METHODS

We sampled fish at ports in two states: Galveston and Freeport, Texas and Venice, Louisiana. In addition, we collected samples with hook-and-line to complement port sampling efforts. To assess annual variation, samples were collected in two years (2002, 2003). Muscle tissue (~20 g) was removed from the dorsal region behind the head, and samples were transported on ice and subsequently frozen. We collected 389 samples from 11 species.

We measured total Hg in fish tissue with a Milestone DMA-80 Direct Mercury Analyzer (Cizdziel et al. 2002). Fish muscle samples were cut into small pieces (about 0.01 - 0.27 g), and each sample was split into two fractions; one was introduced into the machine while the other was dried to determine the water concentration of the tissue. We evaluated water concentration to determine whether dehydration of samples during storage affected measurements of mercury in the wet fraction. We observed no significant dehydration effects; therefore, only wet weight mercury concentrations were reported.

The analytical procedure was calibrated and checked with standard reference materials (Dogfish muscle, Dogfish Liver, Oyster tissue, Lobster hepatopancreas) from the National Research Council of Canada. Sample order was randomized within species. We conducted three replicate measurements on every tenth sample. If inter-replicate variability exceeded 10%, the previous 10 samples were re-analyzed.

From each species, five muscle tissue samples were randomly chosen for stable isotope analysis. Isotope ratios ($^{15}N/^{14}N$) and total nitrogen content were determined using a Finnigan MAT DeltaPlus continuous-flow stable isotope mass spectrometer attached to a Carlo Erba elemental analyzer at the University of Texas at Austin Marine Science Institute. We report isotope ratios in parts per thousand (‰) relative to atmospheric nitrogen, and used delta notation:

$$\delta\ ^{15}N = (R_{sample}/\ R_{standard}\ -1)\times 10^3$$

where $R = {}^{15}N/^{14}N$. A secondary standard reference material (chitin of marine origin, Sigma Aldrich Co., USA, No. C-8908) was used to verify the accuracy of isotopic measurements (Herzka and Holt 2000).

We tested for differences in mercury concentration between years and between states with t-test. For each species, we modeled the relationship between mercury and total length with an exponential equation using regression. We also used an exponential function to model the relationship between mercury concentration and trophic position (as indicated by nitrogen stable isotope values).

RESULTS

In blue marlin, we detected exceptionally high mercury concentrations (mean = 10.59 ppm wet wt, Table 1) that were 10 times the FDA (2001) consumption advisory level (1.0 ppm wet wt). Among the 11 species of pelagic fish surveyed, four had a higher mean mercury concentration than the FDA criterion value, and nine species exceeded the EPA's consumption advisory level (0.3 ppm wet wt, U.S.EPA 2002). Lowest mean mercury levels were found in yellowfin tuna and dolphinfish: 0.18 and 0.07 ppm wet wt, respectively.

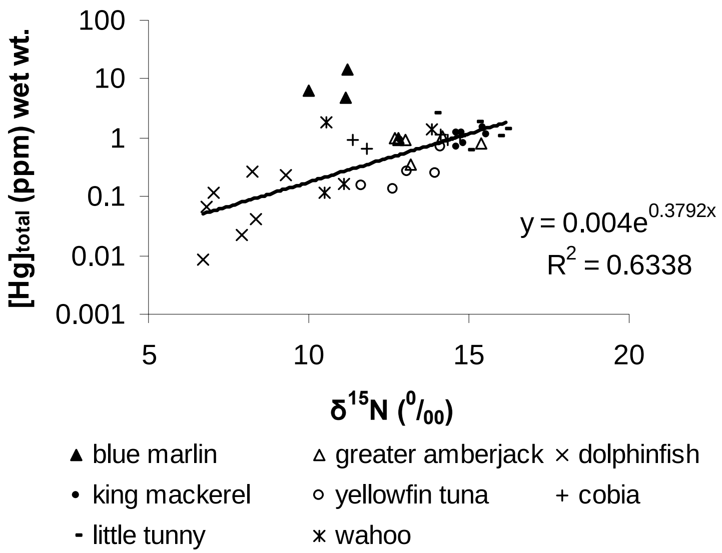
We explored associations between total mercury concentrations and size, and five species showed a statistically significant positive exponential relationship between total mercury concentration and size (Table 2). Blackfin tuna and wahoo had the highest mercury increase rates with size with slope values of 0.081 and 0.046, respectively (Table 2). Due to small sample sizes for blue marlin and swordfish, we did not model mercury versus total length relationships. Greater amberjack (df = 33, t-statistic = 3.05, $p < 0.01$) and yellowfin tuna (df = 58, t-statistic = -6.48, $p < 0.001$) were the only species that showed statistically significant differences in mercury concentration between years, and no species showed significant differences between states (TX vs. LA). Note that we did not examine annual and spatial differences in blue marlin and swordfish due to small sample sizes.

Nitrogen stable isotope values ($\delta^{15}N$) for 8 species that we examined ranged from 6.7 to 16.2 $^0/_{00}$ (Figure 1). Based upon $\delta^{15}N$ values, little tunny had the highest trophic position ($\delta^{15}N$ = 13.9 to 16.2 $^0/_{00}$), king mackerel had the second highest ($\delta^{15}N$ = 12.9-15.5 $^0/_{00}$), and dolphinfish were the lowest ($\delta^{15}N$ = 6.7 to 9.3 $^0/_{00}$). Though they had the highest mercury concentration (mean = 8.37 ppm wet wt), trophic position of blue marlin was intermediate ($\delta^{15}N$ = 10.0 - 11.2 $^0/_{00}$). Excluding blue marlin, there was a significant positive relationship between total mercury and trophic position (expressed as $\delta^{15}N$): $y = 0.004e^{0.3792x}$, where x = $\delta^{15}N$ and y=mercury concentration (R^2 =

Table 1. Total mercury in the muscle tissue of 12 pelagic fish from NW Gulf of Mexico

Species	N	$[Hg]_{total}$ ppm wet wt.	
		mean	SD
blue marlin**	9	10.59	±5.03
Carcharhinid sharks **	9	1.42	±0.45
little tunny**	9	1.08	±0.72
king mackerel*	39	0.96	±0.27
cobia*	17	0.89	±0.52
wahoo*	52	0.76	±0.87
blackfin tuna*	48	0.66	±0.31
greater amberjack*	44	0.6	±0.23
swordfish*	2	0.46	±0.24
yellowfin tuna	103	0.18	±0.15
dolphinfish	57	0.07	±0.09

N = Number of individuals.
** > FDA 2001 human consumption advisory level (1.0 µg/g wet wt.).
* > EPA 2002 human consumption advisory level (0.3 µg/g wet wt.).



0.63).

Figure 1. The relationship between total mercury concentration and trophic position for pelagic marine fishes. An exponential equation was fitted to data from eight species. Blue marlin were not used in the regression.

DISCUSSION

Methylmercury can accumulate from one trophic level to the next with highest concentrations in long-lived top predators (Andersen and Dephledge 1997). Most of the pelagic fishes in this study were apex predators and elevated mercury levels detected in these fish were in accordance with the results of many other mercury studies (Walker 1976, Freeman et al. 1978, Lyle 1984). Among all the other top predator fishes, blue marlin showed an exceptionally high mercury level (10.59 $\pm$ 5.03 ppm). This was 10-fold higher than king mackerel (0.96 $\pm$ 0.27ppm), 18-fold higher than greater amberjack (0.60 $\pm$ 0.23ppm), and 59-fold higher than yellowfin tuna (0.18 $\pm$ 0.15ppm). Yet, the trophic position of blue marlin was intermediate. The reason that blue marlin stood out from all the other species in this study could be due to their long life span and large size. For example, the maximum age and weight ever recorded for king mackerel is 14 years, 40 kg (Collette and Nauen 1983), while blue marlin can live 28 years and grow to 906 kg (Kailola et al. 1993). The long life span may allow blue marlin to accumulate high levels of mercury. In addition, our blue marlin samples were from sport fishing contests, which targeted the biggest individuals in the population. The other species that we examined were smaller and more comparable in size. Mercury levels in swordfish (n = 2, body weight ~ 200 lbs each) were not as high as reported by FDA and EPA, and more data from the Gulf of Mexico are needed to better quantify this pattern. For the other species, we measured mercury concentrations that were similar compared to those recently reported by FDA (2004) and EPA (2004).

Most of the species in the present study exhibited a significant positive relationship between total mercury concentration and size, which is a common observation in fish (e.g. Huckabee 1979, Monteiro and Lopes 1990, Wiener and Spry 1996). For yellowfin tuna, dolphinfish, and king mackerel the slopes of the relationship were nearly identical (0.025, 0.024, and 0.023, respectively, Table 2). The increasing concentration with size results from the very slow rate of elimination of methylmercury relative to the rapid rate of uptake (Huckabee et al. 1979, Trudel and Rasmussen 1997).

The environmental chemistry of mercury is complex, and subtle changes in chemical, physical, biological, and hydrologic conditions can cause substantial shifts in its physical form and valence state over time scales ranging from hourly to seasonal (Amyot et al. 1994, Krabbenhoft et.1998, Lalonde et al. 2002). The entry of methylmercury into the base of the food web and its subsequent trophic transfer in the lowest levels are still poorly understood (James et al. 2003). Reliance on data from total-mercury determinations from trophic levels below fish (including water, seston, plants, and invertebrates) can produce misleading assessments of food-web contamination and erroneous estimates of potential methylmercury transfer to fish and higher trophic levels (Francesconi and Lenanton 1992, Riisgårdand 1986, Watras and Bloom 1992). In addition, many of the pelagic fishes like tuna, little tunny, blue marlin are known to be highly migratory species that migrate to distances far beyond the coast line of Texas and Louisiana (FAO 1994). These processes probably contributed to the lack of differences observed between years and locations.

Table 2. Mercury concentration in muscle tissue (y, mg/g wet weight) of apex predator species in the Gulf of Mexico as a function of total length (x, cm). Significant exponential functions were fitted by regression, and the r-square value (R^2) and size range (minimum and maximum) is listed by species.

Species	Regression Equation	R^2	Min.	Max.
blackfin tuna*	$y = 0.0015e^{0.081x}$	0.74	22.2	81.9
yellowfin tuna*	$y = 0.0094e^{0.025x}$	0.64	54	158.8
dolphinfish*	$y = 0.0065e^{0.024x}$	0.55	38	135.5
king mackerel*	$y = 0.13e^{0.023x}$	0.47	63.5	104.1
wahoo*	$y = 0.0008e^{0.046x}$	0.36	102.9	175.3
greater amberjack*	$y = 0.19e^{0.014x}$	0.15	68.6	111.8
Carcharhinid sharks	Not significant	nd	61	81.3
cobia	Not significant	nd	78.7	147.3
little tunny	Not significant	nd	53.3	68.6

* P-value < 0.05
nd: Not detected

Across species there was a positive exponential relationship between mercury concentration and trophic position. Currently, we are processing more samples to determine whether this pattern holds within as well as across species. The positive effect of trophic position on mercury concentration was also found in many other studies (Walker 1976, Freeman et al. 1978, Lyle 1984, Cabana and Rasmussen 1994, Greenfield et al. 2001). Blue marlin had an intermediate trophic level, and a higher-than-predicted mercury concentration. More samples of blue marlin from a broader size range are needed to better understand why this species did not follow the same trend as the other species that we examined.

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