

Mercury and Selenium in Marine Fishes: Review of a Special Symposium Examining Issues Associated with Fish Consumption and Public Health

Mercurio y Selenio en Peces Marinos: Revision de Una Conferencia Dedicada a la Examinacion de Problemas Asociados con el Consumo de Peces y la Salud Publica

Mercure et Selenium Chez les Poissons Marins: Revue d'Un Symposium Focalise sur les Implications de la Consommation de Poisson pur la Sante Publique

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ABSTRACT

Recent scientific studies have demonstrated selenium's importance in human health and its dietary role in ameliorating mercury's potential toxic effects. Selenium has a high molecular binding affinity for mercury and thus helps to prevent possible mercury toxicity. Although selenium has been known to counteract mercury toxicity since the 1960s, controversy still exists over the inclusion of selenium data in consumption advisories for mercury in fishes. Consideration of selenium in assessing mercury toxicity and the development of a Se-Health Benefit Value are new concepts, not currently in use. To better understand the relevance of these data to fish consumption and public health, a national workshop was held in October 2012 in Point Clear, Alabama, with recognized scientists examining the mercury/selenium issue. A review of that workshop is provided and data on mercury/selenium values and ratios for selected Gulf of Mexico inshore and offshore fishes from Mississippi are presented.

KEY WORDS: Mercury, selenium, marine fishes, public health

INTRODUCTION

The primary exposure of humans to methyl mercury (MeHg) is through consumption of fish (Raymond and Ralston (2004). Current mercury advisories focus on the levels of mercury in fish and do not account for the beneficial nutrients in fish (omega-3 fatty acids) or mercury-selenium interactions. Fish consumption advisories in the U.S. are based, in part, on a study conducted in the Faroe Islands in which neuro-developmental harms occurred in children as a result of maternal consumption of pilot whale and shark meats that had disproportionately high mercury to selenium molar ratios (Julshamn et al. 1987, Nigro and Leonzio 1996). As a result, risks associated with MeHg exposure from eating ocean fish were over-exaggerated. In a contrasting study, one conducted in the Seychelles, the population ate only fish that had high selenium levels and low to moderate mercury levels and there were no detrimental developmental effects in children (Davidson et al. 2011).

Broader understanding of selenium's central role in the seafood safety issue is critical. Current research indicates that the relationship between mercury and selenium is one of "toxicological antagonism" with MeHg toxicity now thought to be due to the negative effect of mercury on selenium physiology (Raymond and Ralston (2004). Under this theory, mercury binds the selenium and prevents the body from creating enzymes that depend on selenium to perform their functions. Thus, MeHg becomes a highly specific, irreversible inhibitor of selenium-dependent enzymes.

Many scientists are now proposing the use of a Selenium-Health Benefit Value (Se-HBV) as a more scientific measure of seafood safety (Ralston 2008). Use of this value is based on strong evidence showing that, regardless of the amount of mercury in a fish, if the selenium level is higher than the mercury, the fish is safe to eat, and the more selenium a fish species contains in relation to mercury, the safer it is. Scientists that oppose the adoption of a Se-HBV at this time note that few studies have been conducted on the Se:Hg ratios in marine fishes in most regions and in those regions that do have data there is variation in the ratios between and within species (Burger 2011).

Mercury and selenium values and ratios are presented for selected species of estuarine and marine fishes commonly consumed in northern Gulf of Mexico coastal communities. Species analyzed included spotted seatrout (*Cynoscion nebulosus*), sand seatrout (*Cynoscion arenarius*), red drum (*Sciaenops ocellatus*), southern kingfish (*Menticirrhus americanus*), striped mullet (*Mugil cephalus*), red snapper (*Lutjanus campechanus*), tripletail (*Lobotes surinamensis*), king mackerel (*Scomberomorus cavalla*), Spanish mackerel (*Scomberomorus maculatus*), Atlantic sharpnose shark (*Rhizoprionodon terraenovae*), and cobia (*Rachycentron canadum*).

APPROACH

Samples of fish for mercury/selenium analysis were collected at fishing rodeos/tournaments and during routine fishery-independent sampling conducted by the Gulf Coast Research Laboratory (GCRL), University of Southern Mississippi.

Twenty individuals of legal harvestable size were targeted for each species. Tissue sampling and data recording protocols developed by the National Seafood Inspection Laboratory (Garrett and Lowery 2006) were followed to allow data to be compared with existing information. For specimens collected by research vessel, the location (latitude and longitude), date, and time of collection, as well as the names of individuals responsible for the collections were recorded. Fish were packed in bags on ice and brought back to the GCRL for processing.

In the laboratory, weight and length (total and standard, fork when appropriate) were recorded for each fish. A two-inch cube of muscle tissue was taken from the area above the left pectoral fin or a two-inch square with maximum depth to the backbone on smaller fish was taken from each fish. The cube was divided in half and the halves bagged separately. One half of the tissue was analyzed for mercury, the other half for selenium. Each tissue specimen was sealed in a small plastic bag and placed inside a larger plastic storage bag with a printed label. All tissue-cube samples were frozen at 4°C for storage and maintained at the GCRL prior to analysis.

Fish sampled at fishing tournaments and rodeos were weighed (total weight) and measured for fork, standard, and total length (depending on the species). These data and other pertinent information, including date, location, and time of catch, if available, were recorded. Tissue-cube samples were collected on site. Each fish sampled had muscle tissue removed in a two-inch cube taken from the area above the left pectoral fin or a two-inch square with maximum depth to the backbone on smaller fish. The cube was divided in half and the halves bagged separately. One half was analyzed for mercury, the other half for selenium. Samples were sealed in a small plastic bag, placed inside a larger plastic storage bag with a printed label, packed in ice, and transported to GCRL. Tissue-cube samples were frozen for storage and maintained at the GCRL prior to analysis.

Analytical work was carried out at the Mississippi Department of Environmental Quality's (MDEQ) Laboratory in Pearl, Mississippi. Tissue cube samples for mercury were analyzed using a direct mercury analyzer (Milestone DMA 80, EPA Bluebook 7473; tissue weight = 0.05 to 0.10 grams; MQL = 0.5 µmoles/kg. Tissue cube samples for selenium were analyzed using an inductively coupled plasma mass spectrophotometer (EPA Bluebook 200.8, method of digestion 3050B (nitric acid); tissue weight = 0.5 to 1.0 grams; Final volume = 50 mls; MQL = 0.63 µmoles/kg). Laboratory analyses were conducted as outlined in an approved Quality Assurance Project Plan (QAPP) and included the use blanks, spikes, and standard reference materials).

RESULTS AND DISCUSSION

Inshore Species

Average and range of values for mercury, selenium and Hg:Se molar ratios for inshore species tested are found in Table 1. Inshore species included striped mullet, southern flounder, sand seatrout, southern kingfish, tripletail, sheepshead, spotted seatrout, Spanish mackerel, gray snapper, and red drum. Average values for selenium exceeded average mercury concentrations for all inshore species tested with average molar ratios below 0.3 mmoles/kg. Individual values for mercury and selenium within a species were variable and levels of mercury in tissue were not always related to size. Highest mercury levels in inshore species occurred in red drum. Values for mercury in red drum were related to size with larger fish having higher concentrations and smaller fish having levels below detection limits. Selenium exceeded mercury levels in all red drum tested, however, a few of the larger fish had molar ratios approaching 1. Lowest values for mercury were found in striped mullet with levels below detection limits in all fish tested; selenium ranged from 1.90 to 7.85 mmoles/kg.

Offshore Species

Values for mercury, selenium and Hg:Se molar ratios for offshore species tested are found in Table 1. Offshore species included blacktip shark, red snapper, wahoo, cobia, blue marlin, king mackerel, yellowfin tuna, dolphin, and Warsaw grouper. Average values of selenium for offshore species were above mercury values and average molar ratios for all species were below 1. As with inshore species, individual values for mercury and selenium within a species varied and levels of mercury and selenium in tissue were not always related to size. Species with individual Hg:Se ratios above 1 included blue marlin, king mackerel, cobia, and wahoo.

Highest mercury levels were found in blue marlin ($n = 11$) and ranged from 4.89 to 60.82 mmoles/kg; selenium concentrations ranged from 12.8 to 52.2 mmoles/kg. Values of mercury and selenium did not appear to be related to size. Average molar ratio approached 1 (0.827) with a range of 0.26 to 1.25. Four of the 11 blue marlin tested had molar ratios in excess of 1. For king mackerel, 40% of the fish tested ($n = 70$) registered mercury levels in excess of selenium. Mercury values ranged from 19.9 mmoles/kg to below the detection limit. Selenium values were more consistent ranging from 6.08 to 12.7 mmoles/kg. Mercury concentrations were highest in larger fish. In general, mercury levels exceeded selenium levels in larger size classes: in the smallest fish (below 94 cm SL) selenium was present in excess of mercury. There was a general trend for higher molar ratios in larger fish, but there was high variability in the larger size classes. Twenty-three percent of the cobia ($n = 31$) had mercury values in excess of

selenium. As with blue marlin, size was not a predictor of mercury and selenium concentrations. Individual values of mercury ranged from 0.75 to 15.25 $\mu\text{moles/kg}$ with selenium values ranging from 3.93 to 11.9 $\mu\text{moles/kg}$. Average molar ratio was 0.721 with individual ratios ranging from 0.15 to 2.66. Mercury concentrations in wahoo exceeded selenium in two of the 13 fish tested. Mercury values were generally higher in larger fish. Molar ratios exceeded 1 in two fish with higher ratios generally seen in larger specimens.

Selenium values in red snapper ($n = 28$) exceeded mercury values in all fish tested. There was a general trend for higher mercury levels in larger fish; selenium levels showed no trend in relation to size. No fish tested had a molar ratio in excess of 1. Selenium values in yellowfin tuna ($n = 30$) greatly exceeded mercury values in all fish tested. Mercury values were higher in larger fish. Individual molar ratios were below 1 with the highest value at 0.327. Selenium values in dolphin ($n = 31$) also greatly exceeded mercury values in all fish tested. Mercury and selenium levels showed no trends in relation to size. Individual molar ratios were below 1 with the highest value at 0.301. Selenium levels in blacktip shark ($n = 12$) were greater than mercury levels in all fish tested. Mercury values were generally higher in larger fish; selenium values were not related to size. Individual molar ratios were below 1 with the highest value at 0.723. Selenium values in Warsaw grouper ($n = 3$) exceeded mercury levels in all fish tested. Molar ratios were well below 1 with the highest value at 0.223.

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Table 1. Values for mercury, selenium, and Hg:Se molar ratios.

Fish Species	N	Hg (avg) $\mu\text{moles/kg}$	Hg Range $\mu\text{moles/kg}$	Se (avg) $\mu\text{moles/kg}$	Se Range $\mu\text{moles/kg}$	Hg:Se (avg) $(\mu\text{moles/kg})$	Hg:Se Range $(\mu\text{moles/kg})$
Striped mullet	15	<0.5	<0.5- <0.5	5.169	1.9 – 7.85	0.107	0.064 – 0.263
Southern flounder	30	0.515	<0.5 – 0.8	7.33	5.19 – 12.5	0.072	0.040 – 0.096
Sand seatrout	30	0.503	<0.5 – 0.6	7.482	3.42 – 11.1	0.071	0.045 – 0.095
Southern kingfish	25	0.538	<0.5 – 0.9	7.773	4.56 – 10.5	0.073	0.048 – 0.154
Tripletail	23	0.517	<0.5 – 0.65	6.090	<0.63–8.87	0.142	0.056 – 0.790
Sheepshead	10	0.630	<0.5 – 1.45	6.017	4.4 – 9.9	0.110	0.066 – 0.266
Spotted seatrout	30	0.717	<0.5 – 1.55	6.389	4.18 – 8.49	0.118	0.059 – 0.360
Yellowfin tuna	30	1.210	0.55 – 3.49	10.049	7.35 – 13.3	0.121	0.050 – 0.327
Dolphin	31	0.863	<0.5 – 2.39	6.999	4.31 – 16.7	0.135	0.030 – 0.301
Spanish mackerel	31	1.019	<0.5 – 3.54	7.018	4.56 – 9.63	0.147	0.057 – 0.430
Gray snapper	30	1.524	<0.5 – 3.39	8.217	6.46 – 10.5	0.193	0.051 – 0.496
Red drum	30	1.995	<0.5 – 5.83	7.251	3.17 – 11.9	0.262	0.059 – 0.869
Blacktip shark	12	2.646	<0.5 – 5.58	8.017	5.45 – 11.7	0.353	0.073 – 0.723
Red snapper	28	3.100	0.75 – 6.7	8.555	5.95 – 12.8	0.363	0.072 – 0.872
Wahoo	13	5.393	0.6 – 10.7	9.675	8.11 – 11.7	0.569	0.063 – 1.152
Cobia	31	4.671	0.75– 15.25	6.658	3.93 – 11.9	0.721	0.150 – 2.660
Blue marlin	11	28.148	4.89– 60.82	31.471	12.8 – 52.2	0.827	0.260 – 1.250
King mackerel	70	8.084	<0.5 – 19.9	8.711	6.08 – 12.7	0.907	0.052 – 2.273
Warsaw grouper	3	1.38	0.95-1.94	9.167	8.36-10.4	0.152	0.114 – 0.223