

## ABSTRACT

A limited set of studies have evaluated the hazards of methylmercury (MeHg) to fish. The range of lowest effect residues reported was 470 ng/g wet weight (ww) to 12,000 ng/g ww based on tissue burdens, and 567 to 54,000 ng/g based on dietary burdens. The measured endpoints ranged from molecular alterations (e.g., metallothionein and testosterone levels) to reproductive impacts (e.g., sex ratio and spawning success). Based on those data, biological effect thresholds that were generated for the determination of risk from MeHg ranged from 323 to 529 ng/g ww based on tissue burdens, and from 345 to 718 ng/g based on dietary burdens. Mercury (total mercury - THg) monitoring data for fish collected from south Florida between 1999 and 2009 were retrieved from the South Florida Water Management District's DBHYDRO database for comparison to the effect thresholds. Six different species comprised that data set: bluegill (Lepomis macrochirus), largemouth bass (Micropterus salmoides), redear sunfish (L. microlophus), spotted sunfish (L. punctatus), eastern mosquitofish (Gambusia holbrooki), and warmouth (L. gulosus). Approximately 20 percent of the data showed THg concentrations greater than the lowest effect threshold concentration for MeHg (323 ng/g ww). A probabilistic approach to risk analysis, which incorporates Monte Carlo sampling of the entirety of both the effects and monitoring data sets, indicated a relatively low likelihood (3.5%) that any individual fish is at risk from MeHg. Segregating the monitoring dataset by species, year, and location revealed that risk varied with each of these factors.

### METHODS

The effect of MeHg upon fish was evaluated by searching the literature for studies that dosed fish with MeHg and documented statistically significant effects. Studies that dosed fish with Hg were not included in this analysis since it is presumed that the majority (~90 percent) of Hg in fish is in the form of MeHg (CH<sub>3</sub>Hg<sup>+</sup>) (USEPA 1997). Only effects that are classified as ecologically important (survival, growth, reproduction, development, behavior) were selected for this analysis (Beckvar et al. 2005). All fish mercury data used in this analysis were retrieved from the South Florida Water Management District's DBHYDRO database for the years 1998-2008. Data for all species except largemouth bass are THg for whole fish. Largemouth bass data are for filets.

Threshold effect levels reported in Table 2 were derived using methods outlined in Beckvar et al. (2005) for effect levels reported in the literature. The simple rank, empirical percentile, and tissue threshold effect level derivations used functions available in Microsoft Excel<sup>®</sup>. The cumulative distribution function derivation was carried out using Crystal Ball<sup>®</sup>.

Risk probability was determined through the Monte Carlo sampling capability of Crystal Ball<sup>®</sup>. It was assumed that the fish monitoring data were lognormally distributed with the shape characterized by the data mean and standard deviation. All risk analyses were based on tissue-based threshold levels since no presumption was made regarding the dietary preferences for the focal species.

Dietary Lowest Effect Residue (ng/g ww)	Tissue Lowest Effect Residue (ng/g ww)	Measurement Endpoint (s)	
		Molecular Level	
3,930	3,557	Decreased testosterone in male fathead minnow (FHM)	Di
870	917	Decreased estradiol in female FHM	Dı
		Tissue Level	
870		Apoptotic follicular cells in FHM ovaries	D
		Organism Level (survival, growth, behavior)	
1,900	470	Decreased mummichog survival	М
987	2,370	Reduced walleye growth	Fr
567	1,310	Reduced GSI in juvenile male walleye	Fr
959	536	Affected schooling behavior in golden shiners	
		<b>Population Level (reproduction)</b>	
870	890	Delayed FHM spawning	D
3,930	4,225	Decreased FHM spawning success	Sa
5,600	1,100	Mummichog sex ratio skewed towards females	Μ
54,000	12,000	Decreased egg fertilization success in mummichog	Μ

# Table 2. Derived Biological Effects Threshold Levels for Protection of Fish

Threshold Derivation	Dietary-based Threshold Levels <sup>2</sup>		
Simple Rank	Lowest "low-effect residue" Highest "no-effect residue"	567 455	
Empirical Percentile	5 <sup>th</sup> percentile <sup>3</sup> 10 <sup>th</sup> percentile <sup>3</sup>	718 870	
Tissue Threshold-effect Level (t-TEL) <sup>4</sup>	t-TEL	345	
Cumulative Distribution Function	5 <sup>th</sup> percentile <sup>5</sup>	275	

<sup>1</sup> From Beckvar et al. (2005)

<sup>2</sup> Units ng/g wet weight as methylmercury

<sup>3</sup> Generated using "percentile" function in Microsoft Excel<sup>®</sup>

<sup>4</sup> Generated using the LER-L (15<sup>th</sup> percentile lowest effect residue) and NEL-M (50<sup>th</sup> percentile no-effect residue). The LER-L and NER-M were 870 and 137 ng/g, and 660 and 215 ng/g for dietary-based and tissue-based threshold levels, respectively.

<sup>5</sup> Percentiles generated using Crystal Ball<sup>®</sup>. The dietary-based level was based on an average of 6,771 ng/g (stdev = 15,754) while the tissue-based level was based on an average of 2,737 ng/g (stdev = 3,500). A lognormal distribution was assumed for both residue data sets.

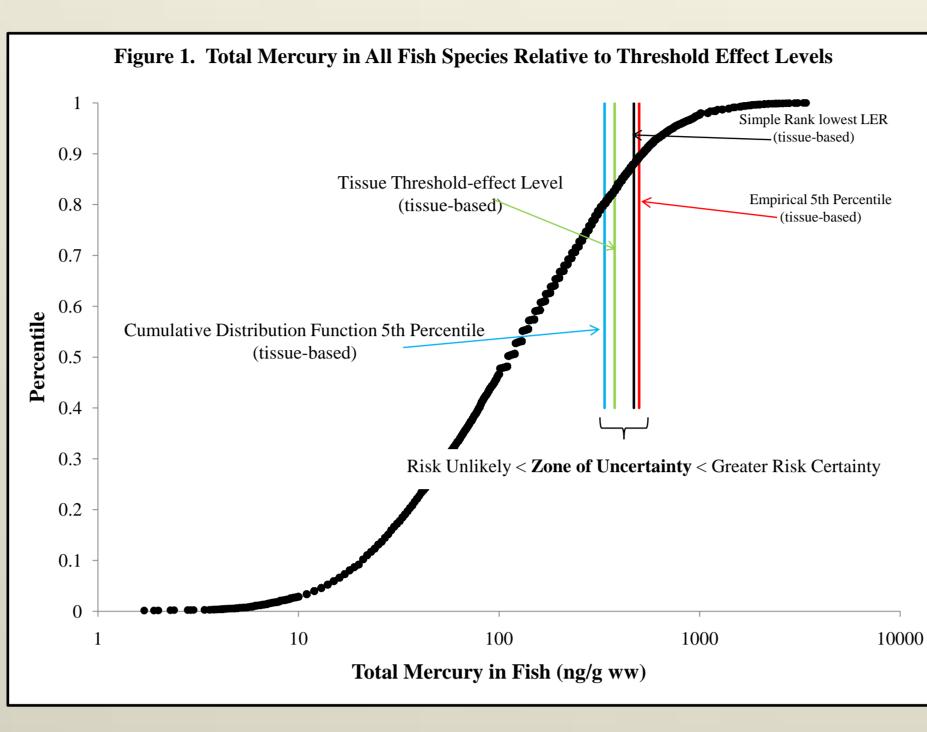
#### **A Risk Assessment of Methylmercury to Fish in South Florida** Tim Bargar - Southeast Ecological Science Center, U.S. Geological Survey, Gainesville, Florida, USA Table 3. Risk Probabilities Based on Monte Carlo Sampling. All Species, All Lo Figure 1. Total Mercury in All Fish Species Relative to Threshold Effect Levels Mosquitofish, All Figure 2. Total Mercury in Fish by Species Relative to Threshold Effect Levels **Red-eared Sunfish, A** mple Rank lowest LER Bluegill **Bluegill**, All Loc 0.9 -Largemouth bass 09 Spotted Sunfish, Al Mosquitofish Tissue Threshold-effect Level Empirical 5th Percentile 0.8 -Redear Sunfish (tissue-based) Warmouth, All L (tissue-based) Spotted Sunfish Largemouth Bass, A 0.7 -Warmouth 06 0.6 Wildlife Criterion T3 fish (77 ng/g) Cumulative Distribution Function 5th Percentile (tissue-based) Location L67F1 0.4 Location HOLYBC 0.3 0.3 Risk Unlikely < **Zone of Uncertainty** < Greater Risk Certainty Zone of Uncertainty 0.2 0.2 -**Location WCA2U3** 0.1 0.1 <sup>1</sup> All scenarios combine residue data among all years (1998-2008). 10000 1000 1000 10000 <sup>2</sup> Data distributions for all scenarios assumed to be lognormal. Total Mercury in Fish (ng/g ww) Total Mercury in Fish (ng/g ww) Figure 3. Tissue Burden Threshold Effect Levels in Relation to Spatial and Temporal Variation of Total Mercury Burdens in Largemouth Bass **Exposure Data** Mercury in Largemouth Bass - G344A 0.9 0.8 07 0.5 Reference Zone of Uncertainty 0.490 ng/g ww 750 -100 120 Total Mercury (ng/g wet weight) in Tissue 250 -2007 1998 2004 2001 L5F1 HOLYBC G342A S5A DISCUSSION 250 -significant effects are reported from the molecular (steroid hormone levels) to the population (skewed sex ratios) levels of biological organization. 1998 2001 2004 2007 2004 2007 1998 2001 2004 1998 2001 2004 2007 1998 2001 ST1W51 G600 by the different threshold levels is unlikely to differ significantly. 1000 750 -· · · · · · · 2006) and tissue (Baeta et al. 2006, Lasorsa and Allen-Gill 1995) will lead to variation in the risk estimation. 1998 2001 2004 2007 1998 2001 2004 2007 ENR302 G606 at the most equal USEPA's guideline levels will be protective of fish in south Florida – provided the effect levels in the literature are accurate. 1250 -..... 1000 750 -X . \_\_\_\_T 3, risk to fish from mercury will also vary spatially and temporally. ...... **Tissue-based** Threshold Levels <sup>2</sup> 2004 2007 1998 2001 1998 2001 Sale -2004 2007 HAN I WCA3F1 G310 objectivity not evident for risk estimation using the LER. 470 1500 1250 440 E E • • • • • • • • likely be manifested as reproductive impairment – absent population adaptation to chronic exposure over multiple generations. 500 1998 2001 2004 2007 2004 2007 529 WCA315 Loxahatchee F4 LITERATURE CITED 1250 Baeta et al. (2006) Total mercury and methylmercury in fish from a tropical estuary. Environ Toxicol V10:183-192. 1000 377 2004 2007 2004 2007 1998 2001 1998 2001 336 WCA3F2 L67F1 WCA2U3 L39F1 Liu et al. (2009) Spatial variability in mercury cycling and relevant biogeochemical controls in the Florida Everglades. Environ Sci Technol V43:4361-4366 1250 -1000 -500 •••••• 250 -**USEPA** (1997) Mercury Study Report to Congress Volume VI: An ecological assessment for anthropogenic mercury emissions in the United States. EPA-452/R-97-008 2004 2007 1998 2001 2004 2007 1998 2001 2004 2007 1998 2001 2004 2007 1998 2001

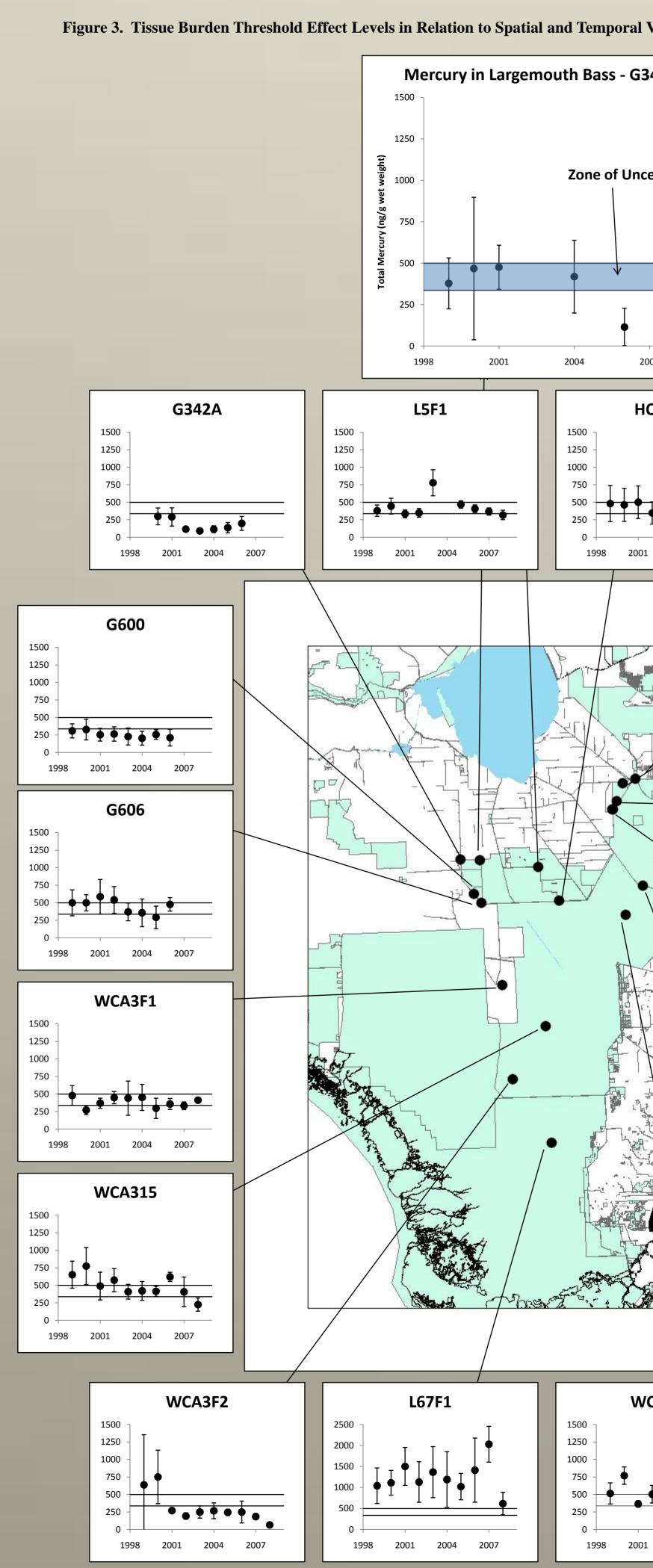
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Drevnick and Sandheinrich 2003 Sandheinrich and Miller 2006 Matta et al. 2001 Matta et al. 2001





nario <sup>1</sup>	Average Total Mercury Whole Fish (ng/g ww)	Standard Deviation	Risk Probability <sup>2</sup>			
ocations Combined	213.9	284.4	3.2			
Locations Combined	28.7	28.5	0.1			
All Locations Combined	73.2	75.4	1.4			
cations Combined	115.2	152.8	1.2			
l Locations Combined	149.7	136.2	1.6			
ocations Combined	175.4	161.6	2.2			
ll Locations Combined	359.6	357.9	7.4			
Largemouth Bass	1,248.1	603.6	36.1			
Bluegill	487.9	395.8	11.1			
Largemouth Bass	630.4	290.2	16			
Bluegill	193.3	122.2	2.1			
Largemouth Bass	545.4	289.2	13.6			
Bluegill	211.9	118.6	2.4			

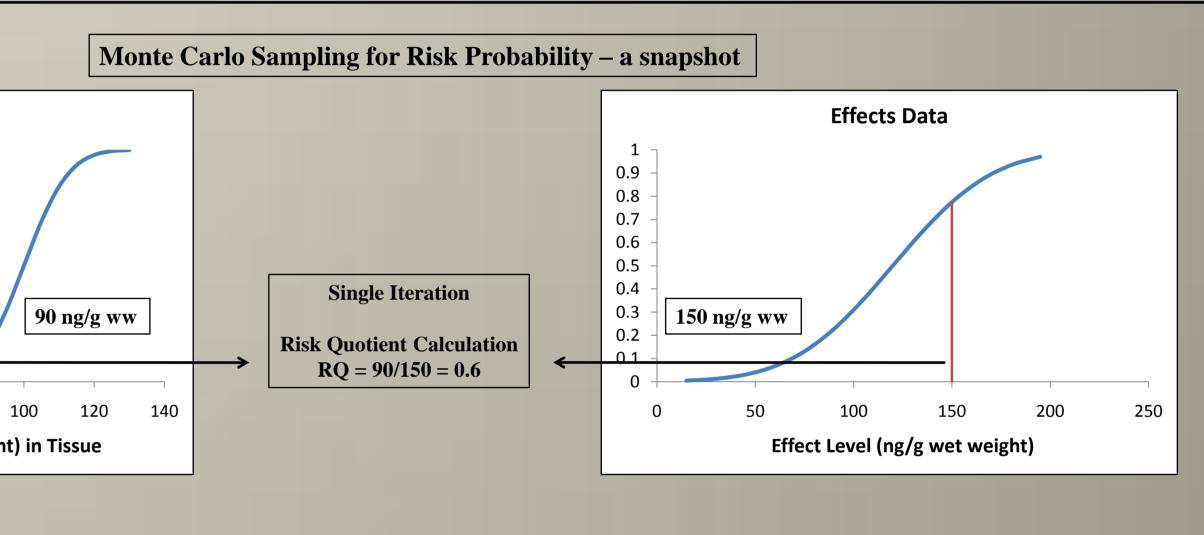


Table 1 reports the effect levels reported in the literature. It is evident from the effects data that sufficient MeHg exposure can adversely affect fish reproduction; statistically

Table 2 presents the different derived Threshold Effect Levels. The premise of the "Threshold Effect Level" is that, if concentrations in the matrix of interest do not exceed the threshold, then risk is unlikely. The "tissue-based" threshold values establish a tissue-based protection level while the "dietary-based" values establish a consumptionbased protection level. The range of derived effect threshold levels based on tissue residue levels (336 - 529 ng/g) is narrow. As a result, the degree of protection afforded

Figures 1 and 2 relate the derived tissue-based lowest-effect residue (LER) levels for MeHg to the THg levels measured in fish. Based on Figure 1, between 11 and 20 percent of the sampled fish in south Florida are at risk. By species, the greatest risk is for largemouth bass while the lowest risk is for mosquitofish (Figure 2). While it is assumed that the majority of the mercury detected in fish is comprised by MeHg, the fact that the actual proportion comprised by MeHg varies with trophic level (Baeta et al.

Figure 2 also indicates the proportion of fish with THg levels that exceed threshold levels for protection of humans and piscivorous wildlife as reported by the U.S. Environmental Protection Agency (1997). Since most of the derived threshold values for fish are greater than those reported by the USEPA, ensuring that THg levels in fish

Figure 3 relates the risk for largemouth bass to location and year. Mercury contamination in fish clearly varies spatially and temporally (Gabriel et al. 2009), which has been reported for other organisms and for the abiotic environment in south Florida (Liu et al. 2009, Rumbold et al. 2002, Gilmour et al. 1998). Concordantly, as shown in Figure

Table 3 reports the probability that fish are at risk from MeHg. Generally, the relative risk among species and locations as indicated by Figures 1 and 2 are reflected by the risk probabilities shown in Table 3. However, the probabilities in Table 3 take into account the variability of mercury residues and effect levels providing a level of

The significance of a risk probability value is often classified subjectively. It could be subject to (1) management considerations, (2) toxic endpoint, or (3) statistical comparison. The levels of risk apparent for fish in south Florida varies widely from almost absent for a species such as the mosquitofish (0.1 percent for all locations and years) to quite apparent for a species like largemouth bass (36.1 percent @ location L67F1). But the risk level is not spatially homogenous with some areas having considerably greater mercury contamination (L67F1 – Everglades National Park) compared to others (ST1W51). At those locations where risk is apparent, the effect will

Beckvar et al. (2005) Approaches for linking whole-body fish tissue residues of mercury or DDT to biological effects thresholds. Environ Toxicol Chem V24:2094-2105 Drevnick et al. (2006) Increased ovarian follicular apoptosis in fathead minnows (*Pimephelas promelas*) exposed to dietary methylmercury. Aquat Toxicol V79:49-54 Drevnick and Sandheinrich (2003) Effects of dietary methylmercury on reproductive endocrinology of fathead minnows. Environ Sci Technol V37:4390-4396 Friedmann et al. (1996) Low levels of dietary methylmercury inhibit growth and gonadal development in juvenile walleye (Stizostedion vitreum). Aquat Toxicol V35:265-278 Gabriel et al. (2009) Annual permit compliance monitoring report for mercury in downstream receiving waters of the Everglades Protection Area: Appendix 3B-1 Gilmour et al. (1998) Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry V40:327-345 Lasorsa and Allen-Gill (1995) The methylmercury to total mercury ratio in selected marine, freshwater, and terrestrial organisms. Water Air Soil Poll V80:905-913 Matta et al. (2001) Reproductive and transgenerational effects of methylmercury or Aroclor 1268 on *Fundulus heteroclitus*. Environ Toxicol Chem V20:327-335 Rumbold et al. (2002) Levels of mercury in alligators (Alligator mississippiensis) collected along a transect through the Florida Everglades. Sci Total Environ V297:239-252 Sandheinrich and Miller (2006) Effects of dietary methylmercury on reproductive hehavior of fathead minnows (*Pimephelas promelas*). Environ Toxicol Chem V25:3053-3057 Webber and Haines (2003) Merucry effects on predator avoidance behavior of a forage fish, golden shiner (*Notemigonus crysoleucas*). Environ Toxicol Chem V22:1556-1561