

Chapter 8

Mercury in Fish

8.1 Results

Lake Michigan fish were collected from April 1994 through October 1995 for total mercury analysis (see Section 2.4.6 for details of the sample collection procedures and Section 2.5.5 for the details of the analysis procedures). Lake trout and coho salmon were collected using gill nets, trawl nets, or other appropriate means. Up to five individual whole fish of the same species and size or age category were combined to produce composite fish samples at each collection. Adult lake trout from 172 to 933 mm in length were collected from three biological sampling areas or biota boxes (see Figure 2-7 in Chapter 2):

- ▶ **Sturgeon Bay biota box** — a combination of three stations (110, 140, and 180) on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- ▶ **Port Washington biota box** — a combination of two stations (240 and 280) in the central Lake Michigan basin near Port Washington, Wisconsin
- ▶ **Saugatuck biota box** — a series of three stations (310, 340, and 380) on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan

Coho salmon were collected in three distinct age classes (hatchery, yearlings, and adult). Coho salmon were collected from various sites selected to follow the seasonal migration of coho, which travel up Lake Michigan tributaries in the fall to spawn. During the summer, coho salmon were collected from the east central and west central regions of the lake. During the fall, coho salmon were collected from the northeastern side of the lake near the Platte River and on the western side of the lake near the Keweenaw River (see Figure 2-7 in Chapter 2). In addition, young coho salmon (hatchery) were collected directly from the Platte River hatchery, where the majority of Lake Michigan stocked salmon originate. Overall, a total of 201 composite samples of lake trout and coho salmon were collected and analyzed for total mercury by cold vapor atomic fluorescence spectroscopy (Table 8-1).

Table 8-1. Number of Composite Fish Samples Analyzed for Mercury

Species-Size Category	Sampling Dates	Number of Composite Samples
Coho-Hatchery	04/21/94 to 04/27/94	5
Coho-Yearling	10/18/94 to 11/16/94	8
Coho-Adult	05/10/94 to 10/25/94	32
Lake Trout	05/12/94 to 10/26/95	156
Total		201

8.1.1 Variation Among Species

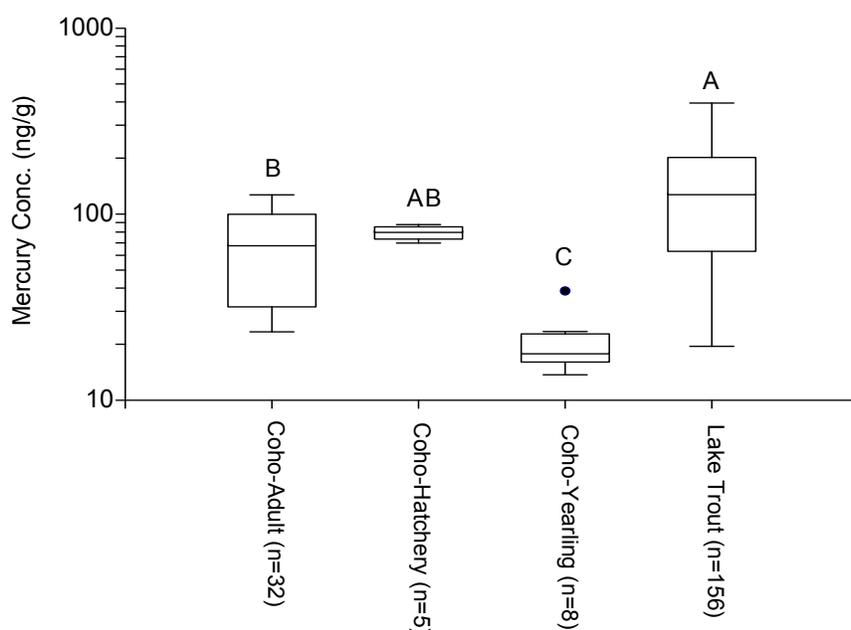
Table 8-2 shows the mean concentration of total mercury (on a wet-weight basis) in Lake Michigan coho salmon and lake trout. Mercury concentrations in adult lake trout ranged as high as 396 ng/g and averaged 139 ng/g. In coho salmon, mercury concentrations ranged as high as 127 ng/g and averaged 79.9, 20.6, and 69.0 ng/g in hatchery, yearling, and adult salmon, respectively. Analysis of variance revealed that mercury concentrations in lake trout were significantly higher than in adult or yearling coho salmon (Figure 8-1). Adult coho salmon also were significantly higher in mercury concentrations than yearling coho, which contained the lowest mean concentration of mercury (20.6 ng/g). Coho salmon collected directly from the hatchery surprisingly contained higher mercury levels (average of 79.9 ng/g) than yearling or adult coho salmon and were not significantly different from lake trout mercury levels.

This is surprising because smaller, younger fish generally contain lower levels of bioaccumulative contaminants than older, larger fish. Among adult coho salmon and lake trout, fish length was highly correlated with total mercury concentrations (see Section 8.1.2). Higher mercury concentrations in hatchery samples than in adult coho may be due to differences in exposures between the hatchery and Lake Michigan or differences in uptake and elimination rates between hatchery and adult fish. Also, given the smaller number of composites of hatchery and yearling salmon, the mean values calculated for these groups may be less representative of their respective populations than mean values calculated for adult salmon and lake trout.

Table 8-2. Mean Total Mercury Concentrations in Lake Michigan Fish (Wet-weight Basis)

Species/Size Category	N	Mean (ng/g)	Median (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Coho-Hatchery	5	79.9	81.2	70.0 to 88.0	6.77	8.48	0
Coho-Yearling	8	20.6	18.1	13.7 to 38.6	7.85	38.0	0
Coho-Adult	32	69.0	69.8	23.3 to 127	35.9	52.0	0
Lake Trout	156	139	130	19.5 to 396	83.8	60.1	0

Figure 8-1. Total Mercury Concentration (Wet-weight Basis) in Lake Michigan Fish



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The trends observed in fish mercury concentrations were the same on a dry-weight basis (Table 8-3). Lake trout contained the highest mercury levels, followed by hatchery, adult, and yearling coho salmon. As with wet-weight basis results, dry-weight mercury concentrations in lake trout were significantly higher than in adult or yearling coho salmon, and mercury concentrations in adult coho salmon were significantly higher than in yearling coho salmon.

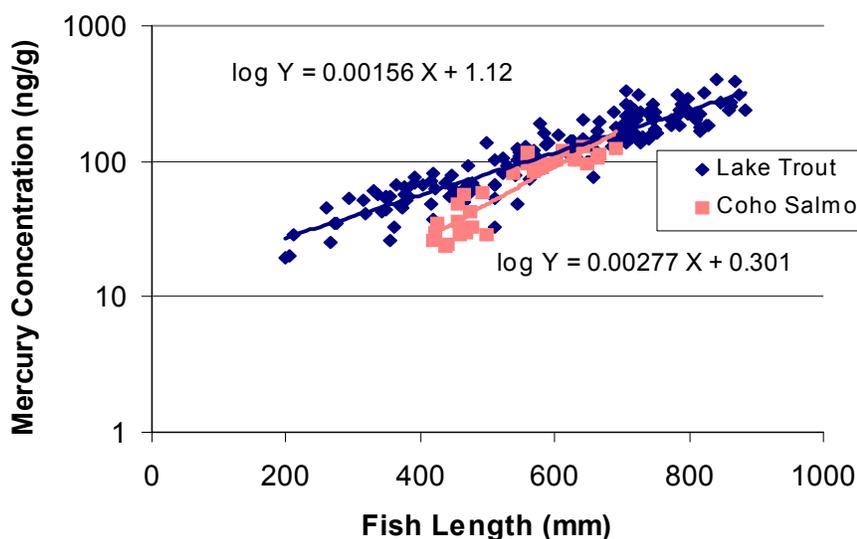
Table 8-3. Mean Total Mercury Concentrations in Lake Michigan Fish (Dry-weight Basis)

Species/Size Category	N	Mean (ng/g)	Median (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
Coho-Hatchery	5	317	331	269 to 344	30.1	9.52	0
Coho-Yearling	8	71.3	57.4	43.1 to 156	36.2	50.7	0
Coho-Adult	32	248	255	98.8 to 504	119	47.9	0
Lake Trout	156	373	341	83.5 to 929	200	53.6	0

8.1.2 Factors Affecting Contaminant Concentrations

Log-transformed total mercury concentrations in Lake Michigan fish were highly correlated ($p < 0.0001$) with fish length and lipid content. Fish length was positively correlated with adult lake trout and adult coho salmon mercury levels with r^2 values of 0.856 and 0.824, respectively (i.e., 85.6% and 82.4% of the variability observed in lake trout and adult coho salmon mercury concentrations are attributable to the fish length). It should be noted that the fish samples analyzed were composites of up to five individual fish. Correlations with fish length reflect the midpoint of the range of fish lengths that were incorporated into the composite sample. It is likely that correlations between contaminant concentrations and fish length would be stronger had contaminant concentrations been measured in individual fish samples, therefore allowing for direct comparison of length and contaminant concentration. Figure 8-2 shows the relationship between fish length and mercury concentrations in Lake Michigan lake trout and coho salmon. Mercury concentrations generally increased exponentially with increasing fish length, producing a linear relationship between fish length and log concentration. Because fish length is often used as a surrogate measure for fish age, this trend indicates either the increased accumulation of pollutants in older fish that have experienced longer duration exposures to mercury, or exposures to higher mercury concentrations.

Figure 8-2. Relationship of Fish Length and Mercury Concentration



Mercury concentrations in Lake Michigan fish also were strongly correlated with fish lipid content ($p < 0.0001$). Lipid content was positively correlated with adult lake trout and adult coho salmon mercury levels with r^2 values of 0.684 and 0.531, respectively. This correlation, however, was likely due to the

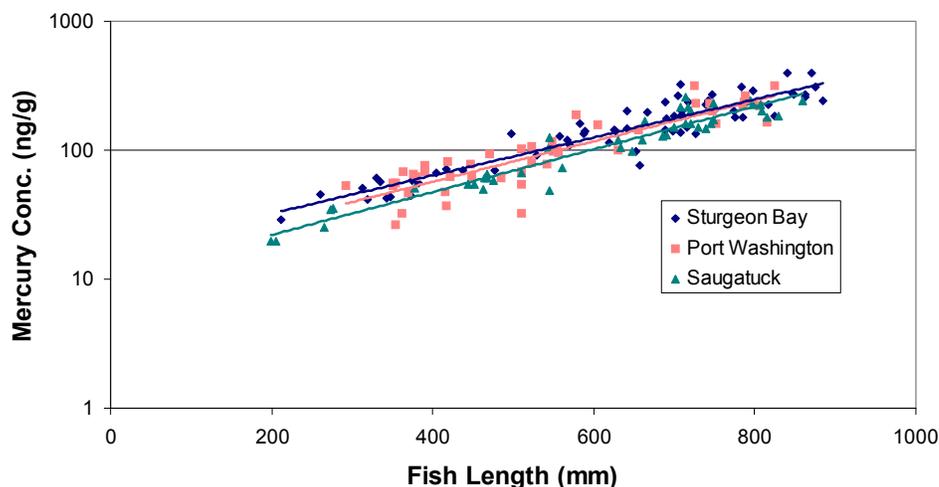
intercorrelation between fish length and lipid content. Lipid content was significantly correlated with fish length ($r^2 = 0.798$ for lake trout; $r^2 = 0.486$ for adult coho salmon), which was in turn correlated with mercury concentration. In general, mercury accumulation in fish is associated with proteins and storage in muscle tissue rather than storage in fatty tissues, where organic contaminants are accumulated, so lipid content is not considered a controlling variable in fish mercury concentrations. In the case of lake trout, multiple regression analysis supported the assumption that lipid content correlation with mercury concentration was a result of the intercorrelation between lipid content and fish length. Multiple regression analysis revealed that mercury concentrations in lake trout were not significantly affected by fish lipid content, when controlling for fish length. For adult salmon, however, multiple regression analysis revealed that mercury concentration was significantly affected by fish length, lipid content, and the interaction of these two factors.

8.1.3 Geographical and Seasonal Variation

Lake trout were collected from three biological sampling areas or biota boxes (Sturgeon Bay, Port Washington, and Saugatuck) during the spring, summer, and autumn months. Two-way analysis of variance (accounting for sampling station and season) revealed that mercury concentrations in lake trout did not differ significantly (at the 95% confidence level) among seasons but did differ significantly among biota boxes. This analysis was not conducted for coho salmon mercury data because coho were collected from various locations throughout the lake, rather than from the designated biota boxes, and coho composite samples occasionally consisted of fish from different sampling sites.

Mercury concentrations in lake trout from the three biota boxes averaged 165 ng/g at Sturgeon Bay, 114 ng/g at Port Washington, and 127 ng/g at Saugatuck. Tukey's multiple comparison test revealed that the mercury concentration in lake trout from Port Washington was significantly lower than in lake trout from Sturgeon Bay. This difference, however, is primarily due to differences in the size of fish collected from the sites. The length of lake trout from Port Washington averaged 536 mm, compared to an average of 629 mm for lake trout from Sturgeon Bay. Because fish mercury concentrations are so strongly correlated with fish length, decreased fish mercury concentrations at Port Washington could be due to the smaller size of fish from this site. Multiple regression analysis was used to evaluate differences between biota boxes while considering fish length. Figure 8-3 compares the mercury versus fish length regressions for fish collected at each of the biota boxes.

Figure 8-3. Total Mercury Concentrations in Lake Michigan Lake Trout of Various Sizes from the Three Biological Sampling Stations



While differences among biota boxes are small, multiple regression analysis determined that the regression intercept for Saugatuck is significantly lower than for the other two sampling locations. When comparing similarly sized fish from the three biota boxes, lake trout from Saugatuck contained significantly lower mercury concentrations than lake trout from Sturgeon Bay or Port Washington.

8.1.4 Bioaccumulation

Mercury is known to accumulate in living organisms at levels far above concentrations in the water column. The degree of this accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

In the LMMB Study, bioaccumulation factors were calculated as the mean dry-weight concentration in fish divided by the lake-wide mean concentration in Lake Michigan. Concentrations of total mercury in Lake Michigan fish were generally 10^5 to 10^6 times higher than total mercury concentrations in Lake Michigan water, which averaged 0.328 ng/L (or 0.000328 ng/g assuming a water density of 1 g/mL). Bioaccumulation factors were 2.18×10^5 for yearling coho salmon, 7.58×10^5 for adult coho salmon, and 1.14×10^6 for adult lake trout. Bioaccumulation factors were not calculated for hatchery coho salmon, because these samples were not collected from Lake Michigan.

The fish species analyzed for mercury content in the LMMB Study (coho salmon and lake trout) represented only top predator fish species. While forage fish species were collected and analyzed for PCBs and *trans*-nonachlor, these species were not analyzed for mercury. For this reason, biomagnification of mercury in the upper pelagic food web could not be assessed. Biomagnification from the lower pelagic food web (plankton) to the upper pelagic food web (fish) is discussed in Chapter 9 of this report.

8.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of fish mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 8-4 provides a summary of flags applied to the fish mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. No results were qualified as invalid, thus all results are represented in the analysis of fish mercury concentrations presented in this report.

Table 8-4. Summary of Routine Field Sample Flags for Fish Mercury

Flag	Number of QC Samples	Percentage of Samples Flagged (%)
EHT, Exceeded Holding Time	—	0.5% (1)
FBS, Failed Blank Sample	44 lab reagent blank samples	0
FDL, Failed Lab Duplicate	153 lab duplicate groups	5% (10)
FMS, Failed Matrix Spike	9 lab matrix spike samples	0
FRS, Failed Lab Reference Sample	24 lab reference samples	0
FSR, Failed Standard Reference Material	24 standard reference material samples	1% (2)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

Few data quality flags were applied to fish mercury data. Of the 201 routine field samples analyzed for mercury, only 1 sample was flagged for exceeding sample holding time, 10 samples were flagged for failed laboratory duplicates, and 2 samples were flagged for a failed standard reference material. The one sample that was flagged for sample holding time exceeded the 1095-day criterion by 3 days. The average holding time for analyzed samples was 680 days.

Field duplicate samples could not be collected for the fish matrix, because individual fish are not expected to contain identical mercury concentrations. Laboratory duplicate samples, however, were prepared by subsampling collected fish samples. Of the 153 laboratory duplicate groups that were analyzed, only 10 exceeded the MQO of 25% relative percent difference (RPD). RPDs for these failed duplicate samples ranged from 25.2% to 31.3%.

A total of 44 laboratory reagent blanks were analyzed to assess the potential for contamination of routine field samples. All of these samples contained less than 1 ng mercury, so no samples were flagged for failed laboratory reagent blanks. Blank sample results ranged from 0 to 0.92 ng, which is more than 4 times below the lowest sample result of 4.1 ng. This indicates no significant contamination of routine field samples.

To evaluate the bias of analytical results, the laboratory analyzed matrix spike samples, laboratory reference samples that consisted of previously analyzed Lake Erie fish, and standard reference materials (SRM) from the National Institute of Standards and Technology. Two SRMs were used for this study: SRM 1566a, an oyster tissue sample with a certified value of 0.0642 mg/kg (no longer available) and SRM 1515, apple leaves, with a certified value 0.044 mg/kg.

No samples were flagged for failed matrix spikes or laboratory reference samples. Recoveries for matrix spike samples ranged from 82% to 109%. Recoveries for laboratory reference samples ranged from 90%

to 115%. Only one standard reference material sample, which was associated with two routine field samples, was flagged for recovery beyond the MQO of 80-120%. This sample achieved a recovery of 133%. Based on the analysis of laboratory matrix spike samples, laboratory reference samples, standard reference materials, laboratory reagent blank samples, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate groups. Table 8-5 provides a summary of data quality assessments for several of these attributes. The results of laboratory duplicate samples revealed good analytical precision for fish data. The mean RPD for laboratory duplicate samples was 11.7%.

Table 8-5. Data Quality Assessment for Mercury in Fish Samples

Parameter	Number of QC Samples	Assessment
Number of Routine Samples Analyzed	—	201
Analytical Precision, Mean Lab Duplicate RPD (%), >MDL	153 lab duplicate groups	11.7%
Analytical Bias, Mean SRM (%)	24 SRM samples	104%
Analytical Bias, Mean LMS (%)	9 LMS samples	92.8%
Analytical Bias, Mean LRS (%)	24 LRS samples	100%
Analytical Sensitivity, Samples reported as <MDL (%)	—	0%

Number of Sample/duplicate pairs used in the assessment is provided in parentheses

SRM = Standard Reference Material

LMS = Laboratory Matrix Spike

LRS = Laboratory Reference Sample

Analytical bias was evaluated by calculating the mean recovery of standard reference material samples (SRM), laboratory matrix spike samples (LMS), and laboratory reference samples (LRS). Results indicated very little overall bias for analytical results. Mean SRM recoveries were 104%, mean LMS recoveries were 92.8%, and mean LRS recoveries were 100%.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the method detection limit. No fish samples were below the detection limit of 0.1 ng/g. The lowest measured concentration in routine field samples was 13.7 ng/g, which is more than two orders of magnitude above the detection limit.

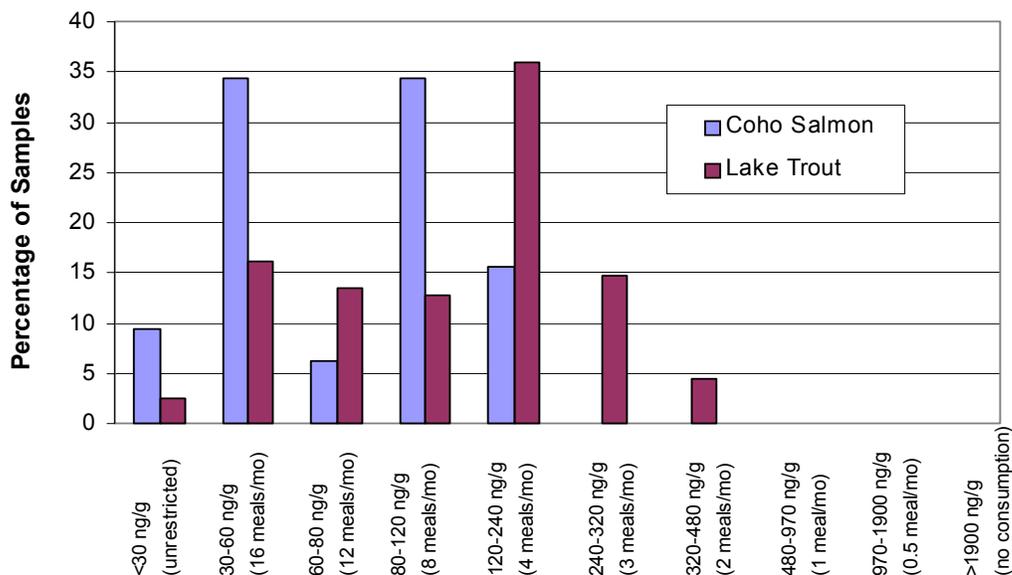
8.3 Data Interpretation

8.3.1 Comparison to Fish Advisory Levels

In the LMMB Study, mercury concentrations averaged 139 ng/g in lake trout and 69.0 ng/g in adult coho salmon. These average values are approximately 10 times below the U.S. Food and Drug Administration's (FDA) action level of 1000 ng/g (1 ppm) for fish tissue content. Even the maximum mercury concentration measured in Lake Michigan fish during the LMMB Study (396 ng/g) was well below the FDA action level. While fish mercury concentrations measured in the LMMB Study do not exceed FDA action levels, these concentrations do warrant restrictions on fish consumption based on EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA, 2000).

Figure 8-4 shows the percentages of coho salmon and lake trout from the LMMB Study that fall into each of the advisory categories recommended by EPA for methylmercury contamination (USEPA, 2000). Since methylmercury was not measured in fish during the LMMB Study, samples were assigned to each category based on the conservative assumption that 100% of total mercury was in the form of methylmercury. Only 3% and 9% of lake trout and coho salmon, respectively, fell into the unrestricted consumption category. The most contaminated coho salmon and lake trout specimens collected in the LMMB Study fell into the 4 meals/month and 2 meals/month restriction categories, respectively. For the average coho salmon sample, EPA guidance would recommend restricting consumption to 12 meals per month; and for the average lake trout sample, EPA guidance would recommend restricting consumption to 4 meals per month. This recommendation is consistent with state-wide advisories for mercury that have been issued by several states. For instance, Illinois has placed a state-wide methylmercury advisory of one meal per week of predator fish to protect sensitive populations (women of childbearing age and children). While Lake Michigan fish mercury concentration warrants some level of fish advisory, few fish advisories in Lake Michigan have been based solely on mercury contamination, because Lake Michigan waters are generally under more stringent fish advisories based on PCB contamination.

Figure 8-4. Percentage of Lake Michigan Coho Salmon and Lake Trout Samples within each EPA-Recommended Fish Advisory Category



Fish advisory categories are based on EPA guidance (USEPA, 2000) and may vary by state. Fish advisory categories also are based on methylmercury concentrations, whereas the LMMB Study data represent total mercury concentrations. LMMB data were assigned to each category based on the conservative assumption that methylmercury contributes 100% of total fish mercury concentrations. Concentrations of mercury were converted to concentrations of methylmercury by multiplying by the ratio of the molecular weights for each mercury species (i.e., 215.625/200.59).

8.3.2 Regional Considerations

Mercury concentrations measured in top predators during the LMMB Study were similar to concentrations measured by other researchers in top predators from the Great Lakes. Rohrer *et al.* (1982) measured mercury concentrations of <100 to 350 ng/g in coho salmon from Lake Michigan tributaries. This is higher than measured in coho salmon during the LMMB Study but is consistent with concentrations measured in the other top predator species (i.e., lake trout). In Lake Ontario, Borgmann and Whittle (1991) found similar mercury concentrations in lake trout. Borgmann and Whittle (1991)

reported an average mercury concentration of 120 ng/g in lake trout collected in 1988. Borgmann and Whittle (1991) also reported that mercury concentrations in Lake Ontario lake trout had decreased steadily to this level from an average of 240 ng/g in 1977. Cappon (1984) measured similar total mercury levels in Lake Ontario lake trout fillets, but much higher concentrations in coho salmon fillets. Mercury concentrations in lake trout fillets ranged from 160 to 290 ng/g and averaged 230 ng/g. Mercury concentrations in coho salmon fillets ranged from 220 to 800 ng/g and averaged 420 and 460 ng/g in two separate fillet cross-sections.

Mercury concentrations of top predators from Lake Michigan were generally lower than those from smaller inland lakes. In a 1999 EPA report on fish mercury data from 1990 to 1995, the weighted mean concentration of mercury in walleye from lakes across Michigan was 375 ng/g (USEPA, 1999b). In a survey of 80 northern Minnesota lakes, Sorensen *et al.* (1990) measured an average mercury concentration of 450 ng/g (range 140 to 1500 ng/g) in a standard 550 mm northern pike. Rose *et al.* (1999) measured an average mercury concentration of 390 ng/g in largemouth bass from 24 lakes in Massachusetts. In a study of 219 Wisconsin lakes, average concentrations of mercury in 450 to 500 mm walleye ranged from 390 to 830 ng/g, depending upon the acid neutralizing capacity of the lakes (Lathrop *et al.*, 1991).

Mercury concentrations in forage fish species were not analyzed in the LMMB Study, so mercury biomagnification within the upper pelagic food web could not be documented. Mercury concentrations measured in top predator species during the LMMB Study, however, were higher than for forage fish species measured by other researchers. Brazner and DeVita (1998) measured mercury concentrations of 9.4 to 31 ng/g in young-of-the-year yellow perch from Green Bay. Mercury concentrations in young-of-the-year spottail shiners from Green Bay ranged from 10.5 to 33.5 ng/g. These concentrations are from 2 to 15 times lower than average mercury concentrations measured in top predators. Similarly, Borgmann and Whittle (1992) measured mercury levels of 37 ng/g and 32 ng/g in 1988 from Lake Ontario smelt and slimy sculpin, respectively.

8.3.3 Factors Affecting Contaminant Concentrations

In the LMMB Study, fish mercury concentrations varied primarily by species and by fish length. Lake trout contained significantly more mercury than coho salmon, and for both species, mercury content increased with fish length. Regression equations to describe mercury content based on the length of Lake Michigan lake trout and coho salmon were calculated, with r^2 values of 0.856 and 0.824, respectively. This correlation with fish length has been well documented and is the basis for size-specific fish advisories. Higher mercury concentrations are accumulated in larger fish because these fish are generally older and have experienced longer exposure durations to environmental concentrations, giving them more time to accumulate pollutants that are not easily degraded or eliminated.

In investigating fish mercury levels in a wide variety of lakes, researchers have identified other lake-specific factors that influence mercury concentrations in fish. Sorensen *et al.* (1990) found that mercury levels in northern pike from Minnesota lakes were correlated with mercury in water, mercury in zooplankton, total organic carbon, iron, and pH (negative correlation). In a study of 219 Wisconsin lakes, concentrations of mercury in walleye increased with increasing fish length and with decreasing acid neutralizing capacity (Lathrop *et al.*, 1991). Mean mercury concentrations ranged from 180 ng/g in the smallest walleye (250 to 349 mm) from high acid neutralizing capacity lakes ($>1500 \mu\text{eq/L}$) to 1470 ng/g in the largest walleye ($>650 \text{ mm}$) from low acid neutralizing capacity lakes ($<100 \mu\text{eq/L}$). Rose *et al.* (1999) measured fish mercury levels in 24 Massachusetts lakes. Mercury concentrations in top predators (largemouth bass) were positively associated with fish weight, lake size, and watershed characteristics. Lake pH was not correlated with mercury concentrations in largemouth bass, but was correlated with mercury concentrations in brown bullhead and yellow perch.