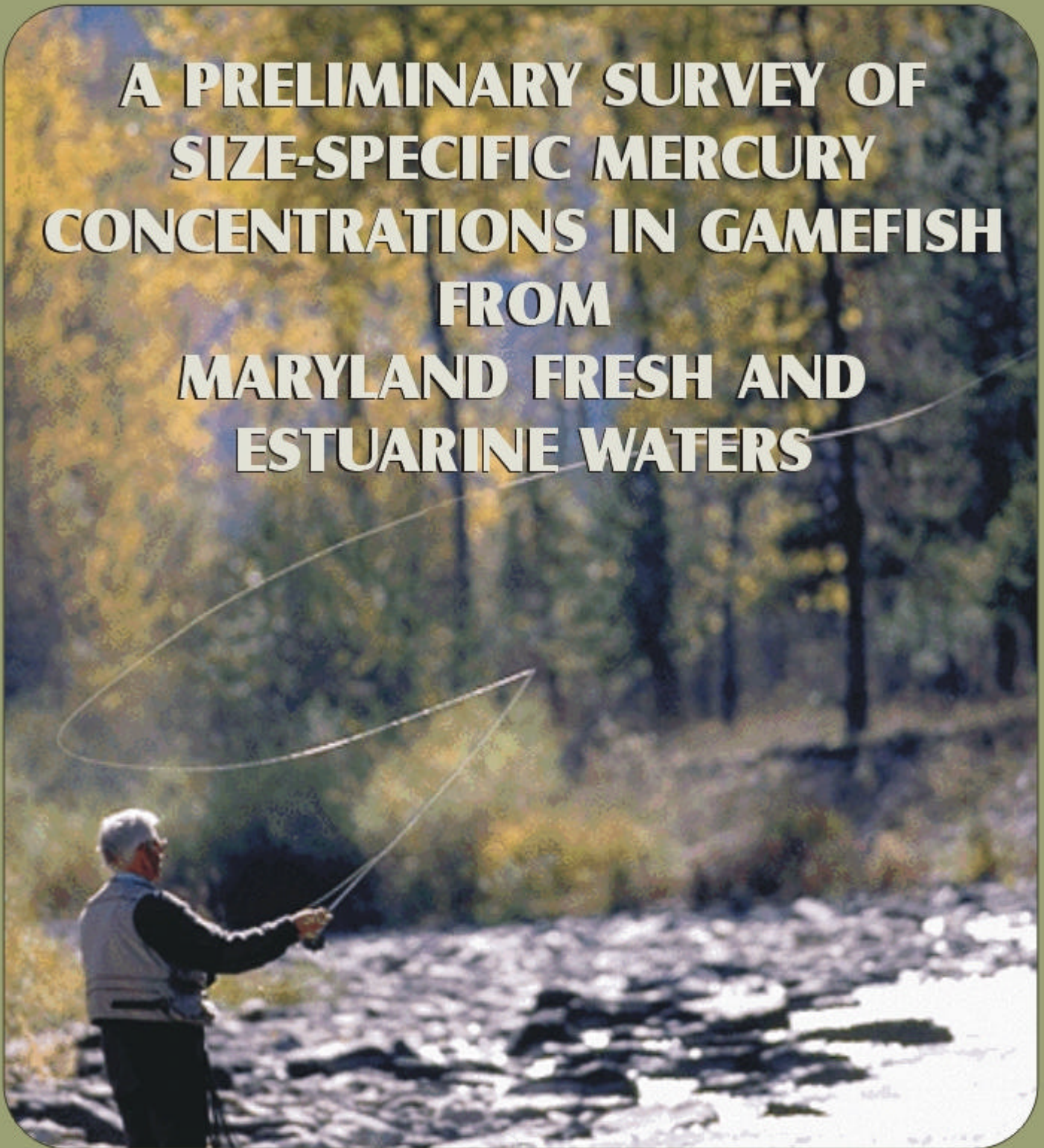


**A PRELIMINARY SURVEY OF
SIZE-SPECIFIC MERCURY
CONCENTRATIONS IN GAMEFISH
FROM
MARYLAND FRESH AND
ESTUARINE WATERS**



**CHESAPEAKE BAY AND
WATERSHED PROGRAMS
MONITORING AND
NON-TIDAL ASSESSMENT
CBWP-MANTA - AD-98-3**



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MERCURY CONCENTRATIONS IN GAME FISH
FROM
MARYLAND FRESH AND ESTUARINE WATERS

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SUMMARY

A preliminary survey of mercury (Hg) levels in game fish from Maryland waters was conducted by the Academy of Natural Sciences Estuarine Research Center (ANSERC) for the Power Plant Research Program of the Maryland Department of Natural Resources. The objective of this study was to make a preliminary estimate of size-specific mercury concentrations in a small number of game fish from a small subset of Maryland fresh and estuarine waters, in order to assess the need for a comprehensive survey of Hg in Maryland fish.

The experiences of other U.S. states and other countries strongly suggest that certain types of water bodies in the state of Maryland will contain fish that exceed recommended advisory levels for Hg. The limited data set presented here show that larger individual striped bass, chain pickerel, walleye, white crappie and largemouth bass in some Maryland fresh waters have mercury tissue levels which are at or exceed a common advisory level for limiting human consumption of fish, while Hg levels in Chesapeake Bay striped bass appear much lower.

In the United States, more fish consumption advisories are posted because of elevated mercury (Hg) concentrations than because of any other contaminant. Elevated levels of Hg in fish are a potential threat to wildlife as well as to human health. There is a broad consensus among mercury experts that the cause of high mercury concentrations in fish today is elevated atmospheric inputs of mercury to lakes and their watersheds. Atmospheric Hg deposition in the mid-Atlantic exceeds that in most other regions of the United States. While there are currently no Hg-based fish consumption advisories posted in Maryland, this work indicates that a more comprehensive study of Hg in Maryland fish is warranted.

There is an extensive body of literature documenting a positive relationship between fish Hg concentrations and fish size within an individual water body. Piscivorous fish also contain higher levels of Hg than do co-existing fishes of lower trophic levels. Therefore, comparisons of fish Hg contamination among water bodies must be standardized to species and body size. Mercury bioaccumulation varies widely among ecosystems. Certain types of ecosystems are more susceptible to Hg bioaccumulation, particularly low pH or highly colored fresh waters. Although atmospheric emissions occur largely in the form of inorganic Hg, it is the organic form, methylmercury (MeHg) that accumulates and causes toxic effects at higher trophic levels. Bioaccumulated MeHg arises primarily from in situ production by natural bacteria in sediments and soils.

In this study we present some of the first information on Hg concentrations in individual fish of known length and/or weight for Maryland. The study examined fish from both freshwater impoundments and from the Chesapeake Bay and its tributaries. Our analysis of Hg in fish was an ancillary part of a larger, PPRP-funded study of Hg cycling in Maryland waters. For this snapshot study, the sampling objectives were to measure Hg in at least 2 species of game fish from each of 3 impoundments, 3 tidal or non-tidal riverine sites, and 3 estuarine sites. For each species/site combination, at least 3 individual fish that varied in size, but represented the larger size classes were to be collected. In general, new fish sampling efforts were not

undertaken for this small project. Rather, most fish were taken from existing DNR and other fish sampling programs, by DNR through anglers, or purchased from watermen. Overall, Hg concentrations in a little over 100 fish from 7 freshwater, 3 tidal and 4 estuarine locations were measured.

The results of this survey are not meant to be a statistically rigorous assessment of Hg levels in Maryland fish; nor does this study provide sufficient information to make decisions about consumption advisories. These data add to the State of Maryland's general survey of contaminants in fish composites by providing size-specific data for Hg in fish; and by providing data on fish from the highest trophic levels and fish from fresh waters. Maryland Department of the Environment's published findings have focused on Chesapeake Bay, but examination of fish in Maryland fresh waters by MDE is underway.

In Maryland, as expected, freshwater fish contained proportionally more Hg at the same size than did fish from Chesapeake Bay. Of the fish examined, the largest freshwater sportfish contained the highest levels of Hg. Most freshwater fish were taken from Deep Creek, Liberty, Cash, and Piney Run Reservoirs. Piney Run and Liberty Reservoirs are impoundments of branches of the Patapsco River in Carroll County. Cash Lake is an impoundment of a branch of the Patuxent, in Prince George's County near the Patuxent Wildlife Research Center. Deep Creek Lake is in Garrett County. It is the largest lake in Maryland (3,900 acres), a reservoir (impounded in 1924) of the Youghiogheny River, and is affected by both acid deposition and acid mine drainage. Low pH and high color (dissolved organic carbon) in lakes are both indicators of potentially elevated MeHg production and bioaccumulation.

Large piscivores from Deep Creek Lake and Liberty Reservoir exceeded the FDA action level of 1 mg Hg/kg fish tissue. Fish in Beaver Run and Cash Lake exceeded a common advisory level of 0.5 mg Hg/kg fish tissue. Both levels are tissue screening levels that are used in evaluating the necessity of a fish consumption advisory for humans. For most fish species in most lakes, Hg concentrations increased with the size of fish. Weight was a better predictor of Hg concentration than fish length. Mercury bioaccumulation in fish varied among freshwater bodies, as measured by differences in the Hg to weight relationships among lakes. By regressing fish length or weight against Hg concentration, the level of Hg contamination in fish can be compared among water bodies within Maryland, and with other jurisdictions.

In Deep Creek Lake, Hg concentrations in chain pickerel appeared quite elevated. Fish over about 0.7 kg exceeded 1 mg Hg/kg fish tissue. Enough pickerel were collected to provide a good relationship between length and Hg concentration, increasing confidence that these fish are representative of the system. Data collected as part of this study were similar to Hg concentrations measured in Deep Creek pickerel by Versar in 1992. However, MDE has reported much lower values for Hg in reservoir fish than those reported by ANSERC and Versar. Mercury concentrations in smallmouth bass from Deep Creek may also be somewhat elevated. Deep Creek Lake has many characteristics that make it a candidate for elevated MeHg production and bioaccumulation (acid deposition and acid mine drainage; high atmospheric Hg deposition; reservoir), and it is a heavily used recreational fishery. Deep Creek Lake should become a focus

of state monitoring efforts for Hg in fish. The one walleye examined from Liberty Reservoir was 48 cm long and contained 0.98 mg Hg/kg.

Panfish were examined in two impoundments, Cash Lake in Prince Georges County and Piney Run Reservoir in Carroll County. Crappie from Piney Run were 6-10 cm longer than crappie with the same Hg concentration in Cash Lake. Large differences in size-normalized Hg concentrations between the lakes highlight the large differences in MeHg production and bioaccumulation among ecosystems. Fairly small crappie in Cash Lake exceeded 0.5 mg/kg, and 20 cm bluegill exceeded 0.3 mg/kg. If there is a sports or subsistence fishery in Cash Lake, this lake should be of particular concern. Mercury levels in fish from Piney Run appear intermediate in Hg content in comparison with other water bodies in Maryland, and throughout the US and Canada. Mercury levels in Piney Run perch were higher than yellow perch taken from Chesapeake Bay.

Striped bass comprised the largest group of fish analyzed (n=47). Large striped bass taken from Liberty and Beaver reservoirs contained Hg tissue concentrations that exceed common advisory levels, and had more Hg at the same size than did Chesapeake Bay striped bass. However, the number of reservoir striped bass sampled in this survey was small. Most striped bass sampled were taken from Chesapeake Bay. This large data set suggests that only very large rockfish in the Chesapeake Bay contain Hg at levels that might warrant further investigation. A more complete analysis of Hg in striped bass from Maryland reservoirs, at least, is certainly needed. No other large game fish from Chesapeake Bay were examined in this study.

A variety of fish from the tidal freshwater and oligohaline Patuxent and Potomac were examined. Of the species examined (largemouth bass, yellow perch, catfish, white perch and croaker), only extremely large largemouth bass (> 4 kg) would be expected to exceed 0.5 mg/kg. Catfish contained the least Hg for their size. This is often the case with omnivorous fish, who may eat lower on the food chain than piscivores of the same size. Largemouth bass and yellow perch taken from these tidal rivers contained less Hg than did the same species taken from Maryland fresh waters impoundments.

Further assessment of Hg levels in Maryland sportfish is needed to protect human and wildlife health. The most important changes to the current State of Maryland fish contaminant sampling strategy should be: 1) an increased sampling intensity in fresh waters that have characteristics putting them at risk for Hg bioaccumulation, 2) targeted sampling of piscivores, 3) size-stratification of fish sampling into three to five relatively narrow size classes and 4) rigorous quality assurance of Hg analytical data including interlaboratory calibrations.

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LIST OF ABBREVIATIONS AND ACRONYMS

AFS	The American Fisheries Society
ANSERC	The Academy of Natural Sciences Estuarine Research Center
CBL	University of Maryland Chesapeake Biological Laboratory
DNR	Maryland Department of Natural Resources
DOC	Dissolved organic carbon
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
FDA	U.S. Food and Drug Administration
FTMN	Fish Tissue Monitoring Network (MDE)
Hg	Mercury
MCM	Mercury Cycling Model (Tetra Tech)
MDE	Maryland Department of the Environment
MeHg	Methylmercury
NRC	National Research Council, Canada
NIST	U.S. National Institute of Standards and Technology
NOAA	U.S. National Oceanic and Atmospheric Administration
PPRP	Maryland DNR Power Plant Research Program
RfD	Reference dose
SRM	Standard Reference Material
UMD	University of Maryland
USFWS	U.S. Fish and Wildlife Service
WHO	World Health Organization

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INTRODUCTION

In the United States, more fish consumption advisories are posted because of elevated mercury (Hg) concentrations than because of any other contaminant. Over 40 states now have posted fish consumption advisories due to Hg bioaccumulation including all 10 southeastern states (U.S. EPA 1995; 1997a,b). Three states have consumption advisories for all lakes (Michigan, Maine and New Jersey). Mercury contamination of fish is also widespread in northern Europe (e.g. Lindquist et al. 1991). A resurgence of interest in Hg contamination of natural waters in the last decade has arisen following the development of methods to measure Hg at ambient levels in natural waters (e.g. Gill and Fitzgerald 1987), and because of increasing awareness of widespread Hg contamination in fish. There is a broad consensus among mercury experts that the cause of high mercury concentrations in fish today is elevated atmospheric inputs of mercury to lakes and their watersheds (e.g. EPA 1997a; Mason et al. 1994). There are currently no Hg-based fish consumption advisories posted in Maryland. Estimates to date of Hg in Maryland fish (MDE, 1988a,b,c; O'Connor 1994) were made as part of screening level studies that were designed to identify a suite of bioaccumulative substances. These studies were targeted toward estuarine fish. The current study presents some of the first information on Hg concentrations in individual fish of known length and/or weight for Maryland. The study examined fish from both freshwater impoundments and from the Chesapeake Bay and its tributaries.

Consumption of fish is the largest source of Hg in the human diet (WHO 1990). The fetus and small child are the target populations, because of their enhanced sensitivity to this neurotoxin and teratogen. In its recent "Mercury Study Report to Congress", EPA (1997a) concluded that the majority of the U.S. population is probably not at risk from consumption of Hg in fish, but that a portion of the population may be. However, EPA also concluded that available data are inadequate to resolve the risks to subpopulations. There is more and clearer evidence that Hg accumulated in wildlife, especially piscivorous mammals and birds, has caused damage to these populations (Zillioux et al. 1993; Royals and Lange 1993; Sundloff et al. 1994; Scheuhammer and Blancher 1994; Halbrook et al. 1994; Spalding et al. 1994; Meyer et al. 1995; Langlois et al. 1995; Wiener and Spry 1996). The Mercury Study Report, one of the most comprehensive available documents on Hg, was mandated by Congress under the 1990 revisions of the Clean Air Act. Its purpose was to assess the risk from Hg to U.S. human and wildlife populations, and to assess the need for further control on Hg emissions in the U.S.

Since the mid-1800's, atmospheric Hg deposition rates have increased approximately 3-5 fold in the US, based on sediment cores (Swain et al. 1992; Benoit et al. 1994), with higher levels in developed areas and around point sources (e.g. Mason 1997a,b). Mercury deposited to aquatic ecosystems can be converted to methylmercury (MeHg) through the action of bacteria in sediments and other anaerobic habitats. It is MeHg that bioaccumulates in food webs. Production rates of MeHg among ecosystems vary as much or more as does atmospheric Hg deposition, so that MeHg bioaccumulation in fish depends not only on how much Hg enters the ecosystem, but on the ability of an ecosystem to convert that Hg to MeHg (Heyes et al. 1999).

The Mercury Cycle

Mercury is introduced into the environment through a variety of human activities and natural sources and it is redistributed over long distances via the atmosphere. Mercury levels in the atmosphere are estimated to be 3-5 times higher than pre-1850 levels (Mason et al. 1994). Much of this atmospheric Hg pool derives from re-emission of anthropogenic Hg which recycles between the ocean, land and atmosphere. An expert panel estimated that approximately 200,000 tons of Hg have been emitted to the atmosphere globally since 1890, of which 95% now resides in soils, 3% in the surface ocean and 2% in the atmosphere (Expert Panel 1994). Because of the long residence times of Hg in the atmosphere (about 1 year) and the large pool of anthropogenically-derived Hg in soils and the surface oceans, response times for fish or sediments to reductions in new Hg emissions may be years to decades.

Based on EPA's recent inventory, combustion sources comprise the largest fraction (85%) of new anthropogenic Hg emitted to the atmosphere in the U.S. (U.S. EPA 1993, 1997a). Manufacturing sources contribute most of the remaining 15%, particularly smelting, Hg reprocessing, chlor-alkali operations, and Portland cement production. In the early 1990's, medical waste incinerators, municipal waste incinerators and utility boilers were roughly equivalent sources that represented the bulk of emissions. Federally mandated controls on incinerators, particularly medical incinerators, have reduced these source terms significantly in the last few years. Batteries are a major source of Hg in municipal solid waste combustion, which is declining due to government and battery manufacturers' efforts to reduce the Hg content of alkaline batteries and to limit the production of mercuric oxide batteries. As regulation of trash burning and medical waste burning are put in place in the U.S., utility boilers are becoming the major remaining source of new atmospheric Hg in the U.S. Coal-fired burners produce most of the utility Hg emissions, because Hg levels are higher in coal than in oil.

One factor that may contribute to elevated Hg levels in Maryland fish is the high level of atmospheric Hg deposition in the mid-Atlantic. Regional average wet flux is 10 to 20 $\mu\text{g Hg/m}^2$ y, depending on distance from sources. This rate is similar to deposition in south Florida, a region with very high levels of Hg in freshwater fish (Ware et al. 1990). Mercury deposition in Maryland is higher than in most other regions of the U.S., where rates range from 3 to 10 $\mu\text{g/m}^2$ y (Mason et al. 1997a).

Atmospheric deposition of Hg to the Bay and its watershed appears to be the main source of Hg to the Chesapeake. Direct measurements of Hg deposition (Mason et al. 1997a) and estimates of riverine inputs (Benoit et al. 1998; Mason et al. 1997b) suggest that direct atmospheric deposition of Hg to the surface of the Chesapeake is roughly equal to riverine influx of Hg. Both long-range and local sources contribute to Hg deposition in Maryland. Higher deposition rates are found closer to local sources. Direct deposition measurements at four sites around the Bay showed higher rainfall-normalized deposition rates downwind from Baltimore than at more rural sites (Mason et al. 1997a). These direct deposition measurements contrast the findings of an earlier PPRP study (Versar 1994) which concluded that there were no localized

effects of power plants on Hg deposition or bioaccumulation. In that study, Hg deposition was modeled based on current information on the atmospheric chemistry of Hg. However, more recent models that predict substantial Hg deposition local to point sources (Constantinou et al. 1995; Mason et al. 1994; Bullock et al. 1997,1998) and studies that have measured local effects directly (e.g. Dvonch et al. 1995; Keeler et al. 1995; Keeler and Hoyer 1997) are consistent with the findings of Mason et al. 1997.

This report does not attempt to link Hg concentrations in fish to specific Hg sources. Source-receptor modeling of this type has generally not been possible for Hg because atmospheric Hg deposition has multiple sources, and because of the confounding influence of ecosystem biogeochemistry on MeHg production and bioaccumulation. We are collaborating with R. Mason at the University of Maryland, Chesapeake Biological Laboratory, to construct Hg budgets for the Patuxent and for Chesapeake Bay, including identification of sources and sinks of inorganic Hg and production and fate of MeHg within the Bay and its watershed (Benoit et al. 1998; Mason et al. 1997a,b; Mason et al. 1999). Sedimentation is the largest sink for Hg entering Chesapeake Bay (Benoit et al. 1998; Mason et al. 1999), although roughly 5% of Hg deposited to the Chesapeake watershed is exported to the ocean (Mason et al. 1999). In the Patuxent, most MeHg is formed within river sediments; while demethylation, fishing and export to Chesapeake Bay are the major loss terms (Riedel et al. 1999; Gilmour et al. in prep.). The Chesapeake may also be a net source of MeHg to the ocean (Mason et al. 1999).

Mercury emissions in the U.S. appear to have declined in the last decade, based on inventories of sources (U.S. EPA 1993, 1997), and this trend is expected to continue as regulations on incinerators are fully implemented. Sediment cores from a few locations also appear to show a decline in Hg deposition since about 1970 (Swain et al. 1992; Benoit et al. 1994), although these data have high levels of associated uncertainty. Most of the atmospheric Hg point sources in the U.S. are concentrated in the mid-Atlantic coast, in the mid-west and in Florida. The fraction of emitted Hg that is deposited locally or regionally around the source is a subject of much debate. However, deposition of Hg in the mid-Atlantic is substantially elevated over the western U.S. (U.S. EPA 1997).

Although atmospheric emissions occur largely in the form of inorganic Hg, it is the organic form, methylmercury (MeHg) that accumulates and causes toxic effects at higher trophic levels. In most aquatic ecosystems, the external supply of MeHg is insufficient to account for the MeHg accumulating in sediments and biota (Benoit et al. submitted; Watras et al. 1994); rather, bioaccumulated MeHg arises primarily from *in situ* production by natural bacteria in anoxic sediments and soils (Compeau and Bartha 1984; Gilmour et al. 1992). Certain types of aquatic ecosystems are naturally susceptible to high levels of MeHg production and bioaccumulation, including wetlands (e.g. St. Louis et al. 1994, 1995; Hurley et al. 1995; Krabbenhoft et al. 1995; Lee et al. 1995; Branfireun et al. 1996; Gilmour et al. in press; Heyes et al. submitted); high dissolved organic carbon (DOC) lakes (Watras et al. 1995) and lakes with anoxic hypolimnia (Henry et al. 1995; Watras et al. 1995b). In addition, the amount of MeHg production and bioaccumulation can be enhanced by anthropogenic changes in ecosystem biogeochemistry. Three examples are reservoir formation (Bodaly et al. 1984, 1997; Johnston et al. 1991; Kelly et

al. 1997; Tremblay and Lucotte 1997), lake acidity due to acid deposition or other factors (Weiner 1988; Weiner et al. 1990; Gilmour et al. 1992; Driscoll et al. 1994), and potentially wetland construction (St. Louis et al. 1994; Heyes 1996).

Factors that affect mercury bioaccumulation by fish

Mercury concentrations in fish are functions of a large number of factors (reviewed by Wiener and Spry 1996). Feeding habits and food chain structure influence accumulation (MacCrimmon et al. 1983; Futter 1994; Cabana et al. 1994) along with ecosystem characteristics that affect Hg methylation rates and Hg loading rates. There is an extensive body of literature documenting a positive relationship between fish Hg concentrations and fish size (e.g. Scott and Armstrong 1972; Wren and MacCrimmon 1983; Wren et al. 1991; Lange et al. 1993,1994; Stafford and Haines 1997). Therefore, comparisons of fish Hg contamination among water bodies must be standardized to species and body size. Piscivorous fish contain higher levels of Hg than do co-existing fishes of lower trophic levels.

Among lakes, acidity and DOC, and the amount of wetland area in a lake's watershed appear to be the most important variables in predicting Hg in fish. A number of studies have shown relationships between low pH and/or high DOC and high levels of Hg in fish (e.g. Wren and MacCrimmon 1983; Greibe et al. 1990; Suns and Hitchin 1990; Cope et al. 1990; Wren et al. 1991; Nilsson and Hakanson 1992; Lange et al. 1993; Fjeld and Rognerud 1993; Haines et al. 1995). The pattern of high Hg levels in low pH and high DOC water bodies is very widespread, found in Europe, South America, Canada and the U.S. (Wiener and Spry 1996). Acid deposition, and more specifically deposition of sulfuric acid, stimulates the microorganisms (sulfate-reducing bacteria), that produce MeHg within sediments (Gilmour et al. 1992), and may also affect MeHg degradation (Winfrey et al. 1987) and bioaccumulation (Watras et al. 1995a). The mechanism whereby DOC affects MeHg accumulation is less clear. Ecosystems with high DOC tend to have high percentages of wetland area, and these are places where microbial Hg methylation is very rapid. DOC may also act as a ligand to keep MeHg in solution and enhance its transport (Hurley et al. 1995). Photochemical degradation of MeHg is an important loss mechanism, and DOC acts as "sunscreen" to prevent that process (Sellers et al. 1996). However, DOC can diminish the uptake of MeHg by organisms from water. Lake size and temperature also affect MeHg bioaccumulation, with more bioaccumulation in smaller warmer lakes (Bodaly et al. 1993). This may be because of enhanced MeHg production in lakes with warmer sediments. In most cases however, pH and DOC appear to be more important variables than lake size (e.g. Wren et al. 1991; Haines et al. 1995).

Wetlands are particularly vulnerable to Hg bioaccumulation because they support high rates of MeHg production (St. Louis et al. 1994; Hurley et al. 1995; Krabbenhoft et al. 1995; Lee et al. 1995; Branfireun et al. 1996; Heyes 1996; Gilmour et al. 1998). Reservoir formation also results in enhanced Hg bioaccumulation because of increased microbial activity and hence microbial Hg methylation after flooding (Kelly et al. 1997). Marine and estuarine waters appear less sensitive to Hg bioaccumulation than fresh waters, because sulfide in sediment inhibits the production of MeHg (Compeau and Bartha 1983, 1985; Craig and Moreton 1983; Gilmour and

Henry 1991; Choi and Bartha 1994; Gilmour et al. 1998; Benoit et al. 1998; Benoit et al. 1999a,b).

Many of Maryland's fresh waters have features that could make them susceptible to high levels of MeHg production and bioaccumulation. Most Maryland fresh waters are impoundments (although most were impounded decades ago) and some are acidified by acid deposition and acid-mine drainage. There are high DOC lakes in the coastal plain. Tidal freshwater and oligohaline areas of estuaries where sulfide accumulation in sediments is relatively low may also be sensitive.

Mercury concentrations in fish

The most contaminated fish have muscle Hg concentrations in the 5-15 mg/kg wet weight range (Wiener and Spry 1996; U.S. EPA 1997b). These are large piscivores found in water bodies affected by aquatic Hg point sources, for example, sites of former chlor-alkali plants (e.g. Henry et al. 1995) or paper mills. Mercury levels in fish may remain high for decades after Hg discharges are stopped (e.g. Rudd et al. 1983). Large piscivores from relatively new reservoirs generally have lower maximum concentrations, 3-4 mg/kg, than contaminated sites. Impoundment of the La Grande 2 reservoir in northern Quebec resulted in increases in Hg in standardized 70 cm pike from 0.6 to 3.0 mg/kg (Verdon et al. 1991). Piscivores in low pH or high DOC ecosystems also range up to 3-4 mg/kg. The Florida Everglades is an example of an ecosystem disposed to MeHg production and bioaccumulation - a warm, high DOC wetland, impacted by high levels of atmospheric Hg deposition (Landing et al. 1995). Approximately 1 million acres of the Everglades system contain largemouth bass with Hg concentrations above 2 mg/kg (Ware et al. 1990; Lange et al. 1993, 1994).

There is a significant body of work showing that nearly all (95-99%) of the Hg accumulated in the upper food web is MeHg. Inorganic Hg does not bioconcentrate through the food web; concentrations in the highest trophic levels are similar to or lower than those at the lowest trophic levels (e.g. Watras et al. 1998). However, MeHg bioconcentrates from each trophic level to the next. The fraction of total Hg that exists as MeHg increases up the food chain, with the lowest percentages in algae and the highest percentages in piscivorous fish, mammals and birds (Watras and Bloom 1992; Bloom 1992; Cleckner et al. 1998). Even at the level of zooplankton, most Hg in the animals is MeHg (see references for many studies in Watras et al. 1998). Within sediments, predatory benthic invertebrates contain Hg mostly as MeHg (Bodaly et al. 1997). In both piscivorous and non-piscivorous fish species, 95-100% of Hg is MeHg (Bloom 1992). This is true even in heavily Hg contaminated systems (e.g. Southworth et al. 1995).

Diet is the primary route of MeHg uptake for fish (Phillips et al. 1980; MacCrimmon et al. 1983; Cope et al. 1990). Although fish may take up MeHg from water passing over the gills, the relative efficiency of uptake by this route is low (about 10%) compared to MeHg in the diet (65 to 80% or greater) (Phillips and Buhler 1978). Once taken up, MeHg in fish is redistributed throughout the body, accumulating in the long term primarily in muscle. Upon exposure, MeHg

concentrations are highest in blood, spleen, liver and kidney. Over time, MeHg is redistributed to muscle and concentrations in the organs decline. Depuration rates from muscle are very low, with typical half-lives ranging from 0.5 to 2 years in freshwater fish (McKim et al. 1976).

Surveys of Hg in game fish generally measure Hg concentrations in muscle (fillets); while surveys that focus on consumption of Hg-contaminated fish by wildlife examine whole body Hg burdens. In lightly contaminated waters, the ratio of Hg concentration in whole body:muscle is fairly constant across water bodies and fish species (Goldstein et al. 1996). For a variety of freshwater species in the Red River (Minnesota and North Dakota), including benthic insectivores, piscivores and omnivores, a general relationship was found where:

$$[\text{Hg}_{\text{muscle}}] = 0.35 + 0.92 [\text{Hg}_{\text{whole body}}]$$

However, it is more difficult to compare whole body and filet Hg values when comparing fish from uncontaminated and contaminated waters because the ratio of Hg in muscle to Hg in liver changes with the level of Hg exposure. When Hg exposure is low, muscle concentrations exceed that in liver, but when Hg exposure is high liver concentrations exceed that in muscle (e.g. McKim et al 1976; Wiener et al. 1984; Barak and Mason 1990; Harrison and Klaverkamp 1990; Al-Hashimi and Al-Zorba 1991; Hornung et al. 1993; Niimi and Kisson 1994).

Hg in Maryland Fish

The State of Maryland examined Hg concentrations in fish as part of a broader Fish Tissue Monitoring Network (MDE, 1988a,b,c). Historically, the Fish Tissue Monitoring Network has examined fish primarily in Chesapeake Bay and its tributaries. The MDE FTMN was designed as a screening level analysis to identify bioaccumulative substances that may present a potential risk to humans. As a result, this program was not designed to provide a mechanism to compare contaminant loads in different waterbodies or identify empirical relationships between fish size and tissue concentrations. Composite samples were used for analysis and data were not normalized to size. The U.S. Fish and Wildlife Service sampled Hg in Maryland fish, including Chesapeake Bay, Potomac, and Susquehanna River sites, as part of the National Contaminant Biomonitoring Program starting in the mid 1970's (Lowe et. al. 1985; Schmidt and Brumbaugh 1990). Like MDE, the FWS examined mean Hg concentrations across sizes. FWS found that mean Hg concentrations in fish did not exceed national 85th percentiles.

Because Hg concentrations increase with fish size, data are collected without regard to fish size should not be used to assess the relative degree of contamination among water bodies or the trends in fish Hg concentration over time. Both the MDE and FWS sampling programs were targeted toward estuarine fish, while freshwater fish are more likely to accumulate MeHg. Therefore, the published MDE and FWS data sets are of limited use in assessing Hg contamination in Maryland fish.

Both MDE (MDE 1990) and the NOAA Status and Trends program (O'Connor 1994) have information on Hg in Maryland shellfish. However, because mollusks are not at the top of

long food chains, they do not generally accumulate unacceptable levels of MeHg. Predatory fish should be the primary target organisms in Hg risk assessments.

METHODS

Study Design

The objective of this study was to make a preliminary estimate of size-specific mercury concentrations in a small number of game fish from a small subset of Maryland fresh and estuarine waters. The results of this survey are not meant to be a statistically rigorous assessment of Hg levels in Maryland fish, nor does this study provide sufficient information to make decisions about consumption advisories. Rather, the data presented here provide a first look at the Hg concentrations in larger individual fish of known length and/or weight. These data complement the State of Maryland's general survey of contaminants in fish composites by providing size-specific data for Hg in fish, and by providing additional data on Maryland fresh waters. These data can be used to help assess the need for a more comprehensive survey of Hg in Maryland fish.

Our analysis of Hg in fish was an ancillary part of a larger, PPRP-funded study of Hg cycling in Maryland waters. In general, new fish sampling efforts were not undertaken for this small project. Rather, most fish were taken from existing DNR and other fish sampling programs, by DNR through anglers, or purchased from watermen. The original scope of work for this study was to measure size and Hg concentration in 2 species of fish from each of 3 impoundments, 3 tidal or non-tidal riverine sites, and 3 estuarine sites. For each species/site combination, at least 3 individual fish that varied in size, but represented the larger size classes, were to be collected. However, we took the opportunity to examine more species, locations, and numbers of fish when they were made available to us. Overall, Hg concentrations in a little over 100 fish from 7 freshwater, 3 tidal and 4 estuarine locations were measured. It is important to note that additional fish were not collected according to a preset design; most fish were collected as part of sampling programs with separate objectives.

Collection of fish for Hg analysis

Fish for Hg analysis were collected by a number of routes. Many were provided by DNR, collected either through their routine sampling programs or through requests to private anglers. Some of the fish used in this study were taken specifically for this study by DNR and ANSERC anglers. Other fish were purchased from a waterman. A summary of water bodies, species, collection dates and sample numbers is given in Table 1. Striped bass collected in 1992 were taken by hook and line by ANSERC. Catfish, yellow perch, white perch, and croaker taken from the Patuxent in 1994 were purchased from a commercial waterman in Benedict. Striped bass from the upper Bay and Potomac in 1994 were provided by DNR. All other freshwater and tidal fish taken in 1994 were caught on hook and line by ANSERC personnel. DNR personnel provided a variety of fish samples in the fall of 1995 and winter of 1996, including angler-caught

largemouth bass from the Patuxent and Potomac; white crappie and bluegill from Cash Lake; angler-caught striped bass and walleye from Liberty and Beaver Reservoirs; yellow perch and black crappie from Piney Run; and pickerel from Deep Creek Lake. Fish collected by ANSERC or purchased were fileted fresh, and then a portion of one filet was frozen. Fish provided by DNR were frozen, either as whole fish or filets. Striped bass from the Upper Bay and Potomac were provided as frozen whole, skin-on, right side filets. All samples were frozen as quickly as possible.

Analysis of Hg in fish

When ready for analysis, filet portions were partially thawed and sub-sampled. Prior to 1995, sub-samples were cut out with a knife. Acid washed (10% HCl overnight) plastic knives were used to trim outside surfaces from semi-frozen fish chunks. Then either slices or the remaining chunk was put into an acid washed polypropylene 60ml jar. Weights ranged between 1 and 5 grams. These chunks were then chopped with the plastic knife into small pieces. In 1995 and after, filets or whole fish were sub-sampled by “coring” a section of filet with a stainless steel apple-corer. The filet core was then trimmed as above so that the cleanest, inner section was digested.

To digest the samples, between 0.5 and 1 g of the filet was transferred via the knife into an acid washed (20% HNO₃ 4days) 50 ml Erlenmeyer flask. Five ml of digest acid (30:75 H₂SO₄:HNO₃) were added. All acids used in digestion or cleaning were screened for Hg content; large lots of low-Hg acids were purchased after testing of available batches. Samples were predigested 1 hr at room temperature and then placed on hot plate. Digestion tubes were capped with marbles to allow escape of digestion gases. Temperature was increased slowly until a boil was reached. Digestion was complete when the red/orange gas was mostly gone and samples were almost clear. After cooling, the samples were brought up to the 50 ml mark on flasks with low-Hg deionized water and 0.5 ml of BrCl were added. Flask and contents were weighed. A small aliquot of digestate, usually 10 to 100 µl, was then analyzed for total Hg as below.

Total Hg analysis was performed by cold-vapor atomic fluorescence (CVAF), with pre-concentration of digested samples on gold traps (similar to Gill and Fitzgerald, 1987; Bloom and Fitzgerald 1988). EPA is in the process of validating this method, which will be Method 1631. ANSERC was one of 10 labs that conducted Method 1631 validation for EPA in spring 1998. Our lab takes part in numerous interlaboratory calibrations to maintain a high level of quality assurance. We have participated in the NRC-CNRC NOAA/9, 10 and 11 trace metal intercomparisons of T-Hg in fish and sediment (Willie and Berman, 1995); in the International Mercury Intercalibration Exercises of total Hg and MeHg in water in 1993 and 1994 (Bloom et al. 1995); and in the Mercury Intercalibration Program (MIP) in 1996. We have fallen within the accepted value range on each occasion. We also intercalibrate routinely in a number of matrices with colleagues at the USGS (Madison, WI), Texas A&M Galveston, and Frontier Geosciences (Seattle, WA). We recently participated successfully in an intercalibration of Hg and MeHg in water and gambusia from the Florida Everglades.

For each set of digestions (about 15 samples), two SRMs, two spikes, two duplicates and two blanks were analyzed. Spikes, duplicates, blanks and SRMs were carried through the entire analysis, including digestion. Three standard reference materials for Hg in tissue were used during analysis of fish, DORM1 (NRC, dogfish muscle) and TORT1 (NRC, lobster hepatopancreas) and 1566a (NIST, oyster tissue). Analyses of SRMs are summarized in Table 1. The average RPD for duplicates across all fish analyses in this study was 15.1 ± 18.7 (n=15). Recovery of a 100 ng Hg spike to 0.5 g of fish tissue averaged 96.5 ± 12.8 % (n=8). Detection limits were determined by the value of the appropriate blank, rather than the instrument, which has a absolute detection limit well under 1 pg. Since the blank value varied with the analysis or experiment, specific detection limits and blank values are summarized for each year of fish analysis in Table 2 below. However, the D.L. for this analysis was generally more than an order of magnitude below the lowest Hg concentrations in fish.

SRM	TORT1	DORM1	1566a
certified value	330 ± 60	798 ± 74	64 ± 7
1996			61 ± 8 (n=13)
1995	330 (n=1)	833 ± 77 (n=13)	
1994	344 ± 64 (n=2)	843 ± 64 (n=2)	

	avg. blank $\mu\text{g/g}$	avg. detection limit $\mu\text{g/g}$
1996	0.00055 ± 0.00097 (n=4)	0.0029
1995	0.00004 ± 0.00006 (n=4)	0.0002
1994	0.00039 ± 0.00008 (n=4)	0.0002

Statistical Analyses

Two statistical methods were used to look for differences in the size:Hg ratio in fish of the same species among water bodies. First, the slopes of the Hg:weight regression were compared among water bodies. Second, analysis of covariance was performed in which Hg concentration was modeled on both fish size and site (Somers and Jackson 1993). Fish weight was a much better predictor of Hg concentration than was fish length, and weight was used in all analyses.

Statistical analysis was performed using SAS 6.11 for Windows. Neither the raw Hg concentration data nor the fish weight data were normally distributed, either across all species and sites, or for most individual species. Although regressions of Hg concentration against fish weight were generally highly significant (again either across all species and sites, or for most individual species), the residuals of regression analyses using untransformed data were generally significant and not normally distributed. Log transformation of weight, length and Hg content allowed analyses that met assumptions of normality. A regression of ln Hg concentration vs. ln weight for all fish analyzed was highly significant ($P < 0.0003$, $n = 97$), but a regression of ln Hg concentration against ln length for all data was not ($P < 0.29$, $n = 106$). All weight, length and Hg concentration data were ln transformed for further analysis, and Hg to weight relationships were used whenever possible.

RESULTS

A total of 112 fish were analyzed, with rockfish (n=47) comprising the largest group. Table 3 lists the fish analyzed, the water body from which they were taken and the year caught. Results are presented and discussed below by water body and by species. The Hg content of fish increases with their age and size. By regressing length or weight against Hg content, the level of Hg contamination among Maryland fish can be compared among the water bodies sampled in Maryland, and with other regions. These size:Hg relationships can also be used to predict the size of fish above which Hg content will be unacceptable for human consumption.

Presentation of data

In this paper, fish tissue Hg concentration data are presented relative to 1.0 and 0.5 mg/kg tissue levels, levels commonly used by US states in setting human consumption advisories for fish. In the United States, fish consumption advisories are issued by the individual states, based on either a human Hg reference dose (RfD), or a fish tissue Hg concentration. The Food and Drug Administration (FDA) Action Level is a tissue screening level of 1.0 mg Hg/kg fish. The Environmental Protection Agency (EPA) recommends that advisories be based on a human Hg reference dose (RfD) of 0.1 µg/kg d (EPA 1997a), which generally leads to higher risk estimates and more conservative advisories. However, new studies of human populations exposed to MeHg in fish may lead to a higher RfD (US EPA 1997a). For example, the Agency for Toxic Substances and Disease Registry adopted a “minimal risk level” of 0.3 µg/kg d in April 1999. The World Health Organization uses 0.47 µg/kg d, a value set in 1990 (WHO 1990). To form an advisory from an RfD, many U.S. states and Canadian provinces (e.g. OME 1997) convert a daily reference dose to a level of Hg in fish that is safe to eat on a weekly or monthly basis. Using the EPA RfD, consumption advisories, especially for children and women of child-bearing age, often begin at or below 0.5 mg/kg. Because of the sensitivity of the fetus and of babies, women who are or who may become pregnant, and nursing women, are advised to eat fish at lower rates than other adults. Of the 33 states that had Hg advisories for fish in 1994, 13 states used the FDA action level as the basis for consumption advisories, and 20 states used methods that resulted in advisories at lower fish tissue Hg concentrations (EPA 1995). A compilation of fish advisories by state is given in U.S. EPA's Listing of Fish Consumption Advisories (EPA 823-C-97-004), a database containing current consumption advisories in the U.S. and Canada. This listing can be found on the world wide web at <http://www.epa.gov/ostwater/fishadvice>. Data include the dates that advisories were issued, the number of water bodies with advisories, and the basis of the advisory.

Table 3. Fish sampled for Hg analysis, showing location, number of fish and (year caught).

	Striped Bass	Lg. Mouth Bass	Sm. Mouth Bass	Yellow Perch	Black Crappie	White Crappie	Bluegill	Pickrel	Walleye
Freshwater Locations									
Liberty Reservoir	4 (95)								1 (95)
Deep Creek Lake			3 (94)					5 (95)	
Piney Run				5 (95)	5 (95)				
Beaver	1 (95)								
Lake Lariat (Calvert Co.)		1 (93)							
Saint Mary's Lake		1 (93)							
Cash Lake						7 (95)	6 (95)		

	Lg. Mouth Bass	Catfish	Yellow Perch	White Perch	Chain Pickerel
Tidal Locations					
Patuxent	2 (95)	6 (94)	3 (94)	3 (94)	
Potomac	9 (95)				
Severn				1 (95)	1 (94)

	White Perch	Croaker	Striped Bass
Estuarine Locations			
Patuxent	4 (93/94)	2 (94)	
Main Bay			10 (93)
Upper Bay			18 (94)
Potomac			14 (94)

Striped Bass

Rockfish comprised the largest group of fish analyzed (n=47). Relatively large fish were collected by ANSERC by hook and line in Chesapeake Bay, near the Bay Bridge in 1992. In addition, fish from the Potomac and upper Bay were provided by MD DNR, which provided frozen fish, plus length, weight and sex data. Four large striped bass from Liberty Reservoir, and one from Beaver, caught in 1995, were also analyzed. Tables 4, 5 and 6 list the Hg concentration in filet (in mg/kg wet weight); plus fish length, weight, date caught and sex where available. For some angled fish, only length or length + girth was provided. In these cases, weight was calculated from the equation:

$$\text{weight (lbs)} = (\text{length} \times \text{girth} \times \text{girth})/800$$

where length and girth are in inches. These fish are noted in the tables; otherwise both length and weight were measured separately.

Figure 1 shows Hg content plotted against length for all striped bass analyzed (note ln:ln scale), including the fish caught in reservoirs. None of the striped bass caught in the Chesapeake Bay, which ranged up to 5.5 kg (or about 12 lbs) in size, exceeded the FDA action level for Hg in fish (1.0 mg/kg). Three fish exceeded 0.5 mg/kg. This value is commonly used as a lower limit for consumption advisories among U.S. states that employ risk-based methods for determination. Both EPA and WHO recommend using a risk-based method, and provide RfDs for MeHg that generally result in advisories at concentrations well below the FDA action level (see introduction). All of the reservoir fish exceeded 0.5 mg/kg, and two equaled or exceeded the FDA action level. It is important to note that the fish from Liberty and Beaver Reservoirs were larger than the fish examined from the Bay, and are therefore expected to contain proportionally higher Hg concentrations.

Nevertheless, analysis of covariance in Hg concentrations, modeled on fish size and site (Somers and Jackson 1993), showed that the reservoir fish had significantly higher Hg concentrations, when adjusted to body weight, than did fish from each of the sites in Chesapeake Bay ($P < 0.04$ for all three comparisons). The assumption of homogeneity of slopes was met for this analysis, as the ln weight by site interaction term and the model residuals were insignificant. There were also differences in Hg accumulation in striped bass among collection sites in Chesapeake Bay. Size-adjusted mercury levels were lower in fish caught in the mainstem Bay off Annapolis in 1992 than in fish caught in the Potomac ($P < 0.001$) and upper Bay ($P < 0.002$) in 1995. These analyses suggest that striped bass in the upper Bay and Potomac accumulated more Hg per unit weight than did striped bass taken near the Bay Bridge. Dilution of water column MeHg concentrations along the salinity gradient of the Bay and its tributaries (e.g. Benoit et al. 1998) might drive the observed differences. The difference does not appear to be based on differences in the weight to length ratios of the fish, as the length to weight ratio for all Chesapeake Bay fish was fairly consistent among all Chesapeake Bay sampling locations (Fig. 3). However, fish were collected in different years.

On average, Chesapeake Bay fish over 8 kg exceeded 0.5 mg/kg, but the average weight at which fish exceeded 0.5 mg Hg/kg ranged from roughly 6 kg in the Potomac to 17 kg in the mid-bay. Data are plotted individually for each site in Fig. 2. The individual weight:Hg relationships for Potomac fish (n=14), and upper Bay fish (n=17), were significant at $P < 0.05$, but the mid-Bay (n=10) and reservoirs (n=5) data sets were not (Figure 1B). The lack of a significant size:Hg relationship for the reservoir fish is not surprising given the small sample size, and that fact that the fish were taken from two water bodies.

The fairly large data set for striped bass in Chesapeake Bay and one of its tributaries shows with some confidence that fish below 8 kg do not generally exceed conservative human consumption advisory levels for Hg. However, higher levels of Hg in a few larger striped bass from reservoirs suggest that a more complete analysis of Hg in striped bass from Maryland reservoirs is needed.

Table 4. Mercury content and other data for upper Chesapeake Bay and Potomac River Striped Bass collected in 1994.

ANSERC ID #	STATE ID #	NOAA CODE	DATE CAUGHT	LENGTH CM	WEIGHT KG	SEX	CATCH LOCATION	Hg MG/KG
1	12PO	173	8/17/94	66.3	3.45	M	POTOMAC RIVER	0.358
2	13PO	173	8/17/94	66.7	3.00	M	POTOMAC RIVER	0.237
3	14PO	173	8/17/94	69.0	3.39	M	POTOMAC RIVER	0.378
4	15PO	173	8/17/94	68.5	3.11	M	POTOMAC RIVER	0.237
5	16PO	173	8/17/94	75.0	4.57	M	POTOMAC RIVER	0.511
6	17PO	173	8/17/94	73.3	4.16	F	POTOMAC RIVER	0.113
7	21PO	173	8/17/94	61.3	1.89	M	POTOMAC RIVER	0.607
8	22PO	173	8/17/94	55.7	1.68	M	POTOMAC RIVER	0.191
9	23PO	173	8/17/94	47.2	0.97	F	POTOMAC RIVER	0.052
10	24PO	173	8/17/94	55.0	1.40	F	POTOMAC RIVER	0.147
11	25PO	173	8/17/94	55.6	1.54	M	POTOMAC RIVER	0.198
12	26PO	173	8/17/94	50.0	1.09	M	POTOMAC RIVER	0.165
13	27PO	173	8/17/94	47.6	1.03	M	POTOMAC RIVER	0.080
14	28PO	173	8/17/94	46.0	0.95	M	POTOMAC RIVER	0.065
15	02UB	025	8/1/94	71.4	3.70	M	UPPER BAY	0.335
16	03UB	025	8/1/94	56.2	1.61	M	UPPER BAY	0.100
17	04UB	025	8/1/94	74.6	4.45	M	UPPER BAY	0.211
18	06UB	025	8/1/94	65.0	2.49	M	UPPER BAY	0.243
19	08UB	025	8/1/94	56.5	1.49	M	UPPER BAY	0.123
20	10UB	025	8/1/94	45.8	0.89	M	UPPER BAY	0.276
21	12UB	080	8/12/94	67.2	3.30	M	UPPER BAY	0.299
22	13UB	080	8/12/94	64.0	2.33	M	UPPER BAY	0.521
23	15UB	080	8/12/94	69.0	3.52	M	UPPER BAY	0.163
24	16UB	080	8/12/94	63.0	2.48	M	UPPER BAY	0.155
25	18UB	080	8/12/94	65.1	2.27	M	UPPER BAY	0.233
26	19UB	080	8/12/94	66.4	3.28	M	UPPER BAY	0.300
27	22UB	080	8/12/94	50.0	1.27	M	UPPER BAY	0.066
28	23UB	080	8/12/94	47.3	0.99	M	UPPER BAY	0.066
29	25UB	080	8/12/94	54.1	1.51	M	UPPER BAY	0.084
30	26UB	080	8/12/94	46.5	1.14	M	UPPER BAY	0.102
31	28UB	080	8/12/94	54.6	1.53	M	UPPER BAY	0.134
32	29UB	080	8/12/94	47.3	1.15	M	UPPER BAY	0.238

Table 5. Mercury content and other data for freshwater Striped Bass collected in 1995.

ANSERC ID# (1994)	DATE CAUGHT	LENGTH cm	WEIGHT kg	CATCH LOCATION	Hg mg/kg
1	11/3/95	111	16.4	Liberty Res	2.932
2	11/4/95		9.1	Liberty Res	0.778
3	11/10/95		3.6	Liberty Res	0.998
4	11/11/95	102	13.0	Liberty Res	0.669
6	10/28/95		5.4	Beaver Run	0.925

Table 6. Mercury content and other data for mid-Chesapeake Bay Striped Bass collected in 1992.

ANSERC ID# (1994)	DATE CAUGHT	LENGTH cm	WEIGHT kg	CATCH LOCATION	Hg mg/kg
1	7/31/92	66	2.94	Bay off Annapolis	0.129
2	10/1/92	84	4.98	Bay off Annapolis	0.221
3	10/1/92	84	5.55	Bay off Annapolis	0.155
4	10/1/92	79	4.30	Bay off Annapolis	0.148
5	10/2/92	66**	2.49	Bay off Annapolis	0.079
6	10/16/92	79	4.76	Bay off Annapolis	0.072
7	10/26/92	66**	2.49	Bay off Annapolis	0.076
8	10/30/92	69	2.72	Bay off Annapolis	0.077
9	10/30/92	74	3.85	Bay off Annapolis	0.228
10	11/7/92	71*	3.80	Bay off Annapolis	0.258

* weight calculated by $((\text{length} \times \text{girth}^2)/800)$

** girth calculated as 1/2 length

Table 7. Regression analysis of striped bass data				
Site	P	r ²	n	regression equation
Overall	<0.0001	0.41	46	$\ln \text{Hg} = (0.80 \times \ln \text{kg}) - 2.4$
Potomac	<0.01	0.45	14	$\ln \text{Hg} = (0.88 \times \ln \text{kg}) - 2.3$
Mid-Bay	<0.12	0.28	10	$\ln \text{Hg} = (0.89 \times \ln \text{kg}) - 3.2$
Upper Bay	<0.02	0.29	18	$\ln \text{Hg} = (0.64 \times \ln \text{kg}) - 2.2$
Reservoirs	NS			

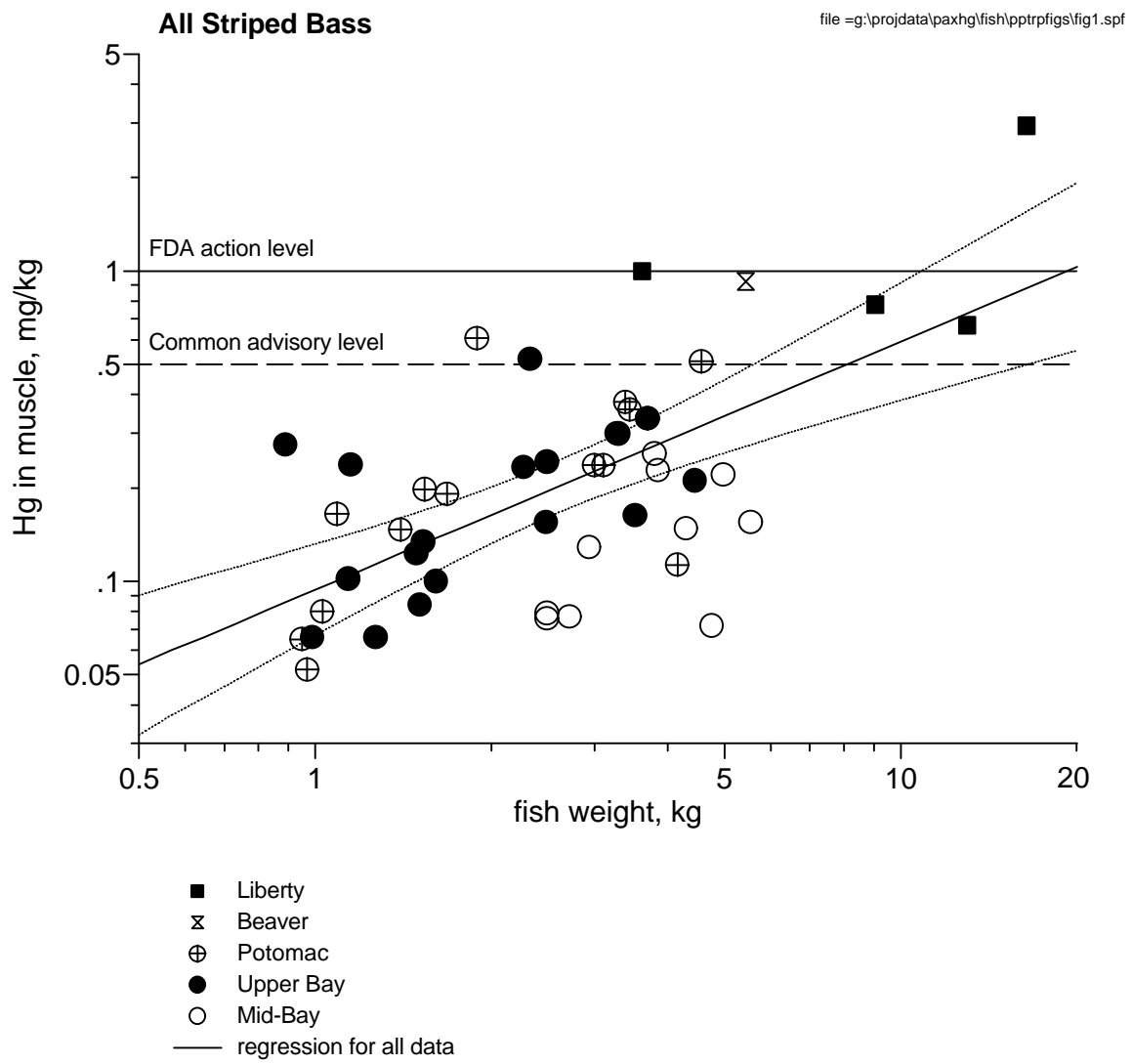
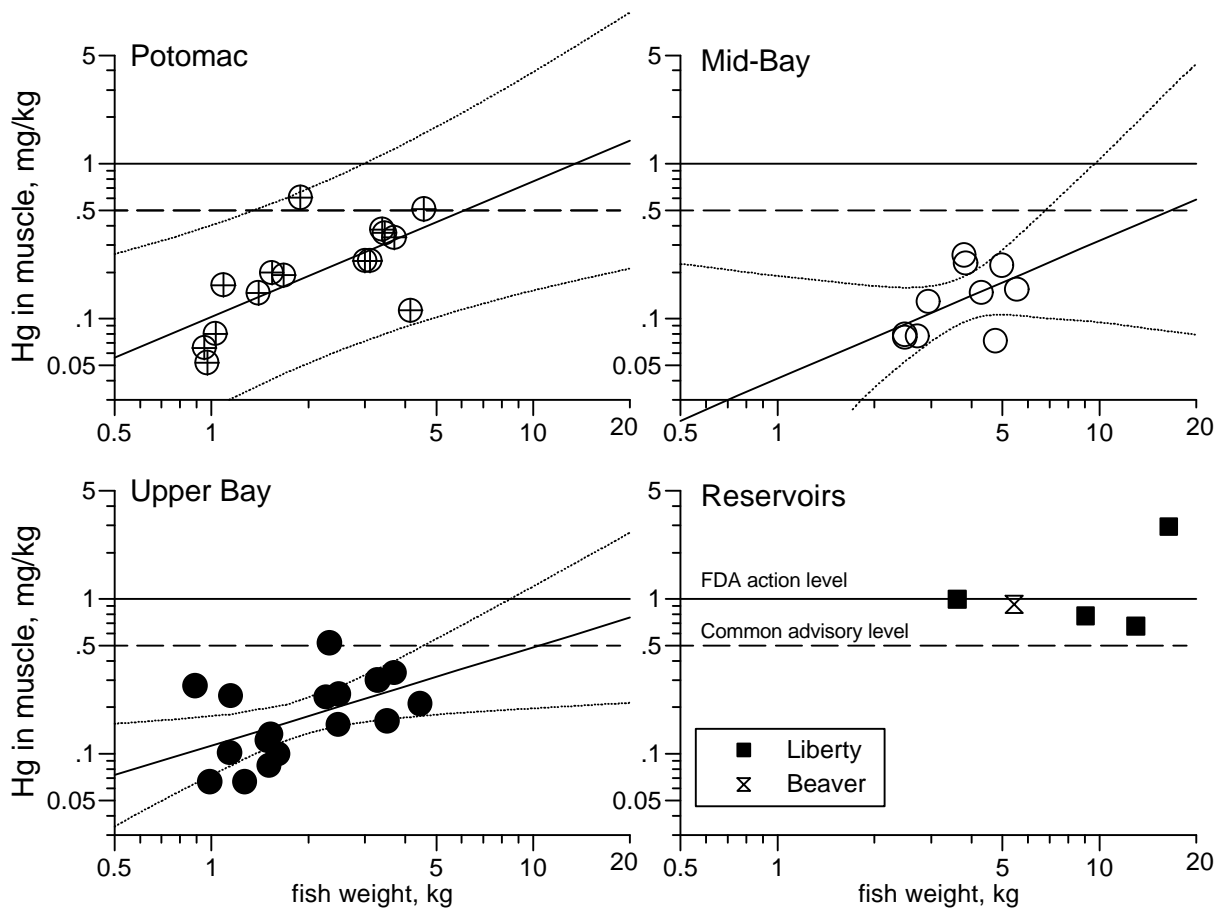


Figure 1. Relationship between ln Hg concentration (mg/Kg) and ln weight (Kg) for all striped bass examined. The solid line and equation represent linear regression of all data shown. Regression data are shown in Table 7, with associated P and r^2 values. Dotted lines represent 95% confidence intervals around the mean.



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Figure 2. Relationships between ln Hg concentration (mg/kg) and ln weight (kg) for striped bass collected in the Potomac River, two areas within Chesapeake Bay, and MD reservoirs. Solid lines are linear regressions of each data set; equations for the regressions are given for each site in Table 7. Dotted lines represent 95% confidence intervals around the mean.

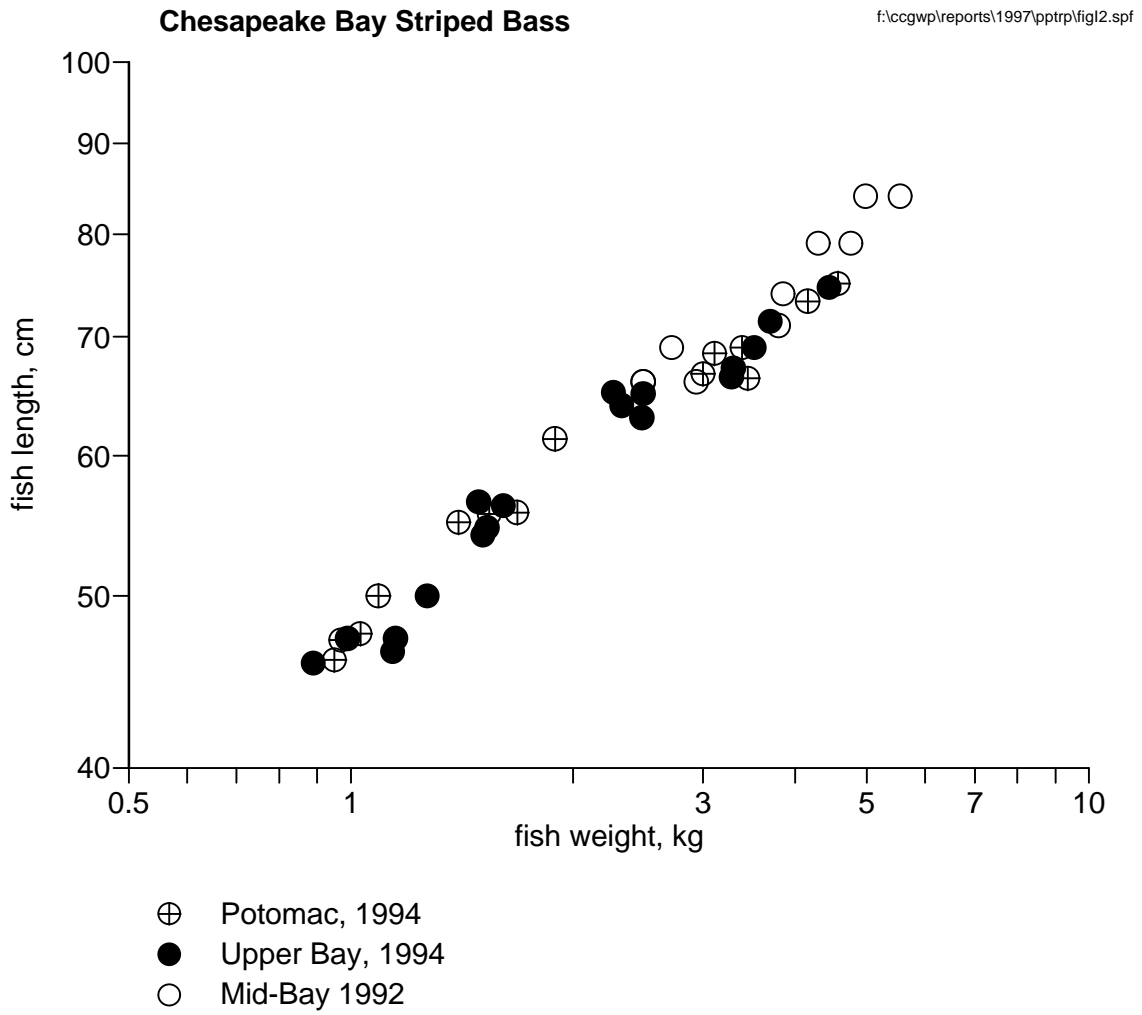


Figure 3. Relationships between length (cm) and weight (kg) for striped bass collected in the Potomac River and two areas within Chesapeake Bay.

Fish in tidal fresh waters and upper estuaries

A variety of species from the tidal freshwater and oligohaline Patuxent and Potomac were examined. Catch location and other data are listed in Tables 8 and 9, and weight vs. Hg concentration is shown in Fig. 4. The expected general increasing trend in Hg concentration with fish size can be seen for all species, but is especially apparent in the larger piscivorous species like largemouth bass. Of the species examined in these rivers, catfish contained the least Hg for their size. Omnivorous fish, who may eat lower on the food chain than piscivores of the same size, often contain lower Hg concentrations. There was also no significant relationship between Hg concentration and weight for catfish.

The data set for largemouth bass from the Potomac was large and wide enough in size range to give a significant weight to Hg concentration regression (Fig. 5; Table 10). Based on the regression, only very large fish (above 4 kg) would exceed 0.5 mg/kg. Only two Patuxent largemouth were examined, but they fit into the same range of size and Hg concentration. Bass taken from the Patuxent and Potomac contained less Hg than did bass from Maryland fresh waters (see below). A few white perch and croaker in the 0.2 to 0.4 kg range contained 0.05 to 0.15 mg Hg/kg, although there was one very high outlier at 0.3 kg and

Table 8. Mercury content and other data for fish caught in the estuarine Patuxent and Severn Rivers, 1994-5.

ANSERC ID # 94	RIVER	SPECIES	DATE CAUGHT	LENGTH CM	WEIGHT KG	CATCH LOCATION	Hg MG/KG
1	PAX	CATFISH	3/10/94	46	0.924	NOTTINGHAM	0.107
2	PAX	CATFISH	3/10/94	39	0.700	NOTTINGHAM	0.195
3	PAX	CATFISH	3/10/94	48	1.204	NOTTINGHAM	0.052
4	PAX	CATFISH	3/10/94	29	0.336	NOTTINGHAM	0.030
5	PAX	CATFISH	3/10/94	32	0.336	NOTTINGHAM	0.082
6	PAX	CATFISH	3/10/94	32	0.336	NOTTINGHAM	0.031
7	PAX	YEL PERCH	3/10/94	29	0.476	NOTTINGHAM	0.177
8	PAX	YEL PERCH	3/10/94	31	0.560	NOTTINGHAM	0.149
9	PAX	YEL PERCH	3/10/94	27	0.308	NOTTINGHAM	0.110
10	PAX	WH PERCH	3/10/94	20.5	0.168	NOTTINGHAM	0.072
11	PAX	WH PERCH	3/10/94	20	0.168	NOTTINGHAM	0.125
12	PAX	WH PERCH	3/10/94	20.2	0.168	NOTTINGHAM	0.072
15	PAX	WH PERCH	9/22/93	26	0.308	BENEDICT BRIDGE	0.402
17	PAX	WH PERCH	5/18/94	24	0.192	BENEDICT BRIDGE	0.098
18	PAX	WH PERCH	5/18/94	22.5	0.167	BENEDICT BRIDGE	0.112
19	PAX	WH PERCH	5/18/94	22.5	0.159	BENEDICT BRIDGE	0.098
20	PAX	CROAKER	5/18/94	27	0.289	BENEDICT BRIDGE	0.063
21	PAX	CROAKER	5/18/94	24	0.172	BENEDICT BRIDGE	0.044
25	SEVERN	CH PICKEREL	9/94	22.5			0.167
33 (95)	SEVERN	WH PERCH	5/95	25.4	0.34		0.063

Table 9. Mercury content and other data for fish caught in the tidal freshwater Patuxent and Potomac Rivers, 1995-1996.

ANSERC ID # 95/6	RIVER	SPECIES	DATE CAUGHT	LENGTH CM	WEIGHT KG	Hg MG/KG
22	PATUXENT, JUG BAY	LM BASS	10/31/95	39	1.11	0.227
23	PATUXENT, JUG BAY	LM BASS	10/31/95		1.52	0.124
24	POTOMAC	LM BASS	4/24/96	47.2	1.65	0.262
25	POTOMAC	LM BASS	4/24/96	50.2	1.99	0.203
26	POTOMAC	LM BASS	4/24/96	50.5	2.04	0.319
27	POTOMAC	LM BASS	4/24/96	45.2	1.43	0.189
28	POTOMAC	LM BASS	4/24/96	45.5	1.47	0.154
29	POTOMAC	LM BASS	4/24/96	51	2.11	0.258
30	POTOMAC	LM BASS	4/24/96	55.1	1.59	0.189
31	POTOMAC	LM BASS	4/24/96	46	1.81	0.187
32	POTOMAC	LM BASS	4/24/96	42.3	1.25	0.135

All Species Patuxent and Potomac, Oligohaline and Tidal Fresh

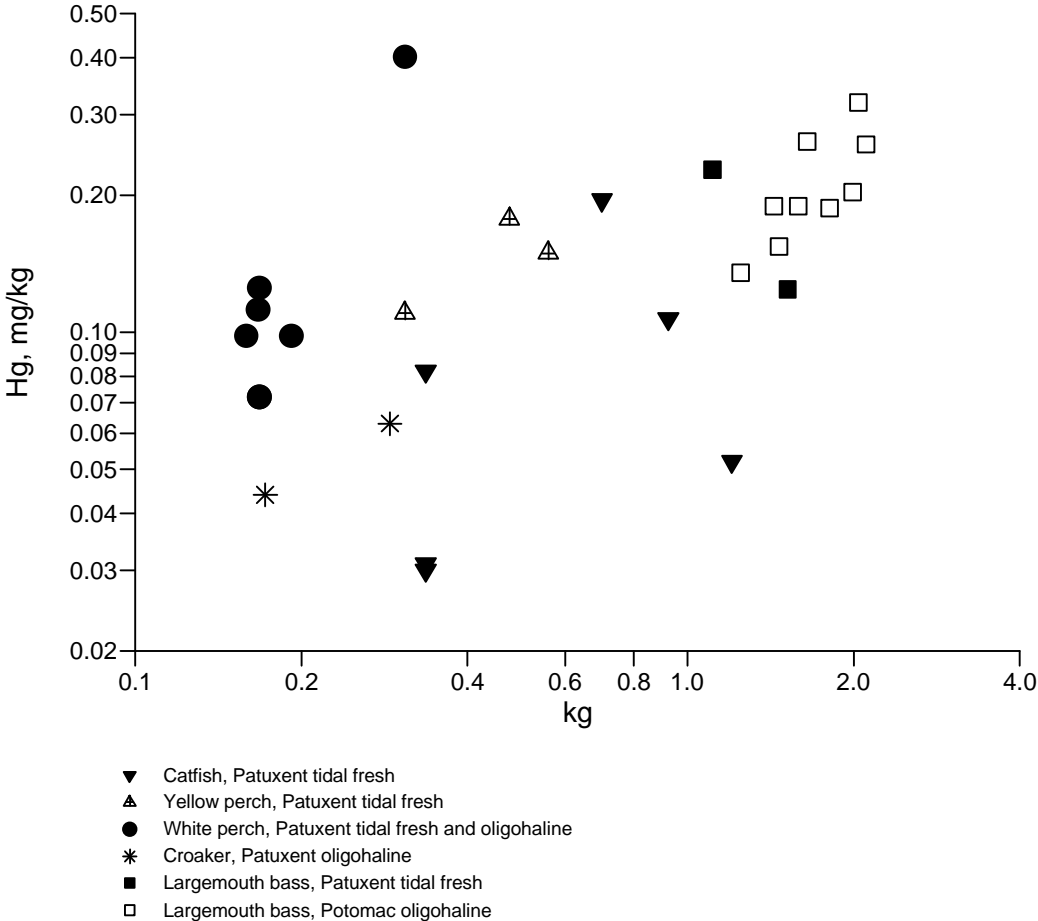
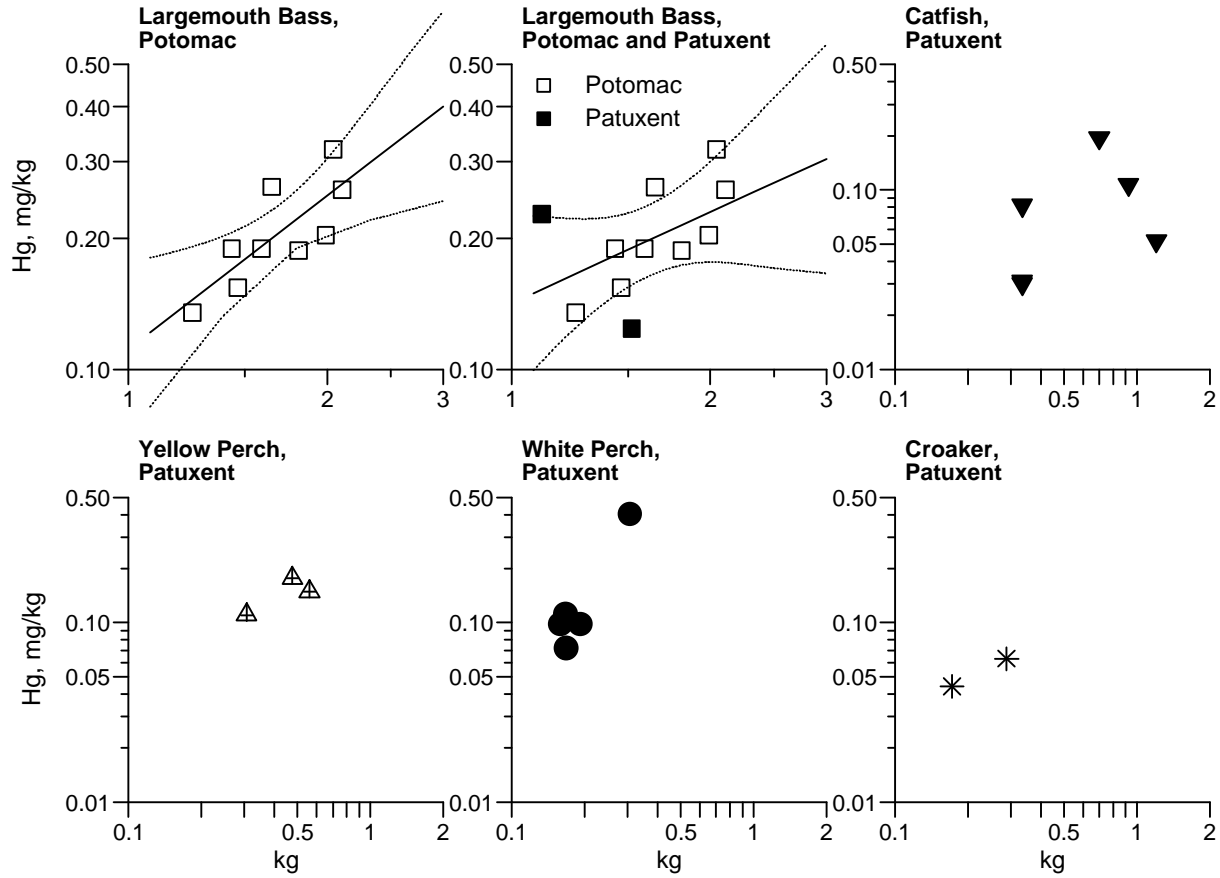


Figure 4. Relationships between ln Hg concentration (mg/kg) and ln weight (kg) for all species examined in the oligohaline and tidal Patuxent and Potomac Rivers.



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Figure 5. Individual relationships between ln Hg concentration (mg/kg) and ln weight (kg) for each species examined in the oligohaline and tidal Patuxent and Potomac Rivers. Solid lines are linear regressions of each data set where P < about 0.1; equations for the regressions are given below, along with P and r² values for each. Dotted lines represent 95% confidence intervals around the mean. Note the different scales among species.

Table 10. Regression analysis of tidal freshwater largemouth bass.				
Site	P	r ²	n	regression equation
Potomac	<0.01	0.62	9	ln Hg = (1.2 X ln kg) - 2.2
Potomac and Patuxent	<0.12	0.25	11	ln Hg = (0.72 X ln kg) - 2.0

0.4 mg Hg/kg. Yellow perch over a somewhat wider size range appeared to increase in Hg with size, but fish up to 0.5 kg did not exceed 0.2 mg Hg/kg. Like largemouth bass, yellow perch taken from the Patuxent contained less Hg than did yellow perch from Maryland fresh waters (see below).

Fish in Maryland fresh waters

Sample locations, species, sizes and Hg content for fish (excluding striped bass) examined from Maryland fresh waters are listed in Table 11. Most fish were taken from Deep Creek, Liberty, Cash, and Piney Run Reservoirs. Piney Run and Liberty Reservoirs are impoundments of branches of the Patapsco River in Carroll County. Cash Lake is an impoundment of a branch of the Patuxent, in Prince George's County near the Patuxent Wildlife Research Center. Deep Creek Lake is in Garrett County. It is the largest lake in Maryland (3900 acres), an impoundment (1924) of the Youghiogheny River, and is affected by both acid deposition and acid mine drainage. Deep Creek is sensitive to acid inputs because of the relatively poor buffering capacity of the sediment and watershed. Lake alkalinity in the early 1980's was <10 mg/L CaCO₃, although pH remained between 6 and 7; surface water sulfate concentrations ranged from 10 to 30 mg/L (Ferrier and Biedka 1985). These reservoirs represent three geologic provinces within Maryland: Cash Lake, St. Mary's Lake and Lake Lariat lie in the Coastal Plain; Liberty and Piney Run Reservoirs in the Piedmont; and Deep Creek in the Appalachian Plateau. Like water bodies in the Appalachian Plateau, streams and impoundments in the coastal plain, especially in southern Maryland, are sensitive to acid deposition because of poorly buffered soils (Knapp et al. 1988). For example, St. Mary's Lake, which is a highly colored lake in St. Mary's county, exhibits large pH swings (4.5 to 9.5) on seasonal cycles. Soils in the Piedmont are well-buffered.

Data are presented graphically in Figs. 6-12. All data are plotted as fish size (X axis) against Hg concentration in filets (Y axis). Size is plotted as weight where weight data were provided; however, weights were not available for fish from some lakes. Data for all freshwater fish examined in this report, except striped bass, are summarized in Fig. 6 (by length) and Fig. 11 (by weight). The increase in Hg concentration with fish size is apparent from these graphs. The highest Hg concentrations were found in large piscivores: walleye, chain pickerel and striped bass (see Fig. 1 for striped bass data). Data for individual species by lake are plotted individually in Figs. 7 to 10 and Fig 12, and discussed below. Although there are differences in the size: Hg concentration ratios among species, there also appear to be large differences among water bodies. Differences in MeHg bioaccumulation between lakes may be a function of differences in the catchment or food web structure, in the net rate of MeHg production between the lakes, or differences in Hg deposition.

Small sportfish in Cash Lake and Piney Run Reservoir. Small sportfish (white crappie and bluegill) in Cash Lake contained more Hg per unit weight than did small sportfish (black crappie and yellow perch) in Piney Run Reservoir (Figs. 7,8). A 23 cm white crappie in Cash Lake exceeded 0.5 mg/kg. The regressions between Hg concentration and both weight (Fig. 12)

Table 11. Mercury content and other data for fish caught in Maryland fresh waters, 1994-1996.

ANSERC ID # 94	LAKE	SPECIES	DATE CAUGHT	LENGTH CM	WEIGHT KG	Hg MG/KG
14	L. LARIAT	CRAPPIE	6/93	26	0.168	0.088
16	ST. MARYS L.	LM BASS		28	0.28	0.489
22	DEEP CREEK L.	SM BASS	8/94	29.5		0.218
23	DEEP CREEK L.	SM BASS	8/94	30		0.309
24	DEEP CREEK L.	SM BASS	8/94	32		0.219
ID #95/6						
5	LIBERTY	WALLEYE	12/18/95	48		0.975
7	PINEY RUN	YEL PERCH	12/4/95	29.5		0.135
8	PINEY RUN	YEL PERCH	12/4/95	30.8		0.288
9	PINEY RUN	YEL PERCH	12/4/95	26.1		0.095
10	PINEY RUN	YEL PERCH	12/4/95	29.7		0.179
11	PINEY RUN	YEL PERCH	12/4/95	29.1		0.186
12	PINEY RUN	BLK CRAPPIE	12/4/95	29.3		0.174
13	PINEY RUN	BLK CRAPPIE	12/4/95	26		0.116
14	PINEY RUN	BLK CRAPPIE	12/4/95	28.5		0.337
15	PINEY RUN	BLK CRAPPIE	12/4/95	25.6		0.092
16	PINEY RUN	BLK CRAPPIE	12/4/95	29.5		0.099
17	DEEP CREEK L.	CH PICKEREL	2/18/96	53.5	1.06	2.137
18	DEEP CREEK L.	CH PICKEREL	2/18/96	45	0.54	0.786
19	DEEP CREEK L.	CH PICKEREL	2/18/96	38.5	0.41	0.300
20	DEEP CREEK L.	CH PICKEREL	2/18/96	38.5	0.37	0.310
21	DEEP CREEK L.	CH PICKEREL	2/18/96	40	0.42	0.187
33	CASH L.	WH CRAPPIE	11/21/95	23	0.166	0.512
34	CASH L.	WH CRAPPIE	11/21/95	19	0.08	0.197
35	CASH L.	WH CRAPPIE	11/21/95	19.8	0.097	0.273
36	CASH L.	WH CRAPPIE	11/21/95	20	0.1	0.320
37	CASH L.	WH CRAPPIE	11/21/95	19.9	0.105	0.250
38	CASH L.	WH CRAPPIE	11/21/95	19	0.097	0.258
39	CASH L.	WH CRAPPIE	11/21/95	19.9	0.113	0.345
40	CASH L.	BLUEGILL	11/21/95	20.4	0.137	0.327
41	CASH L.	BLUEGILL	11/21/95	19.6	0.138	0.318
42	CASH L.	BLUEGILL	11/21/95	18.9	0.156	0.187
43	CASH L.	BLUEGILL	11/21/95	20.9	0.142	0.244
44	CASH L.	BLUEGILL	11/21/95	19.9	0.131	0.152
45	CASH L.	BLUEGILL	11/21/95	18.9	0.119	0.194

**All freshwater sportfish
(except striped bass), by length**

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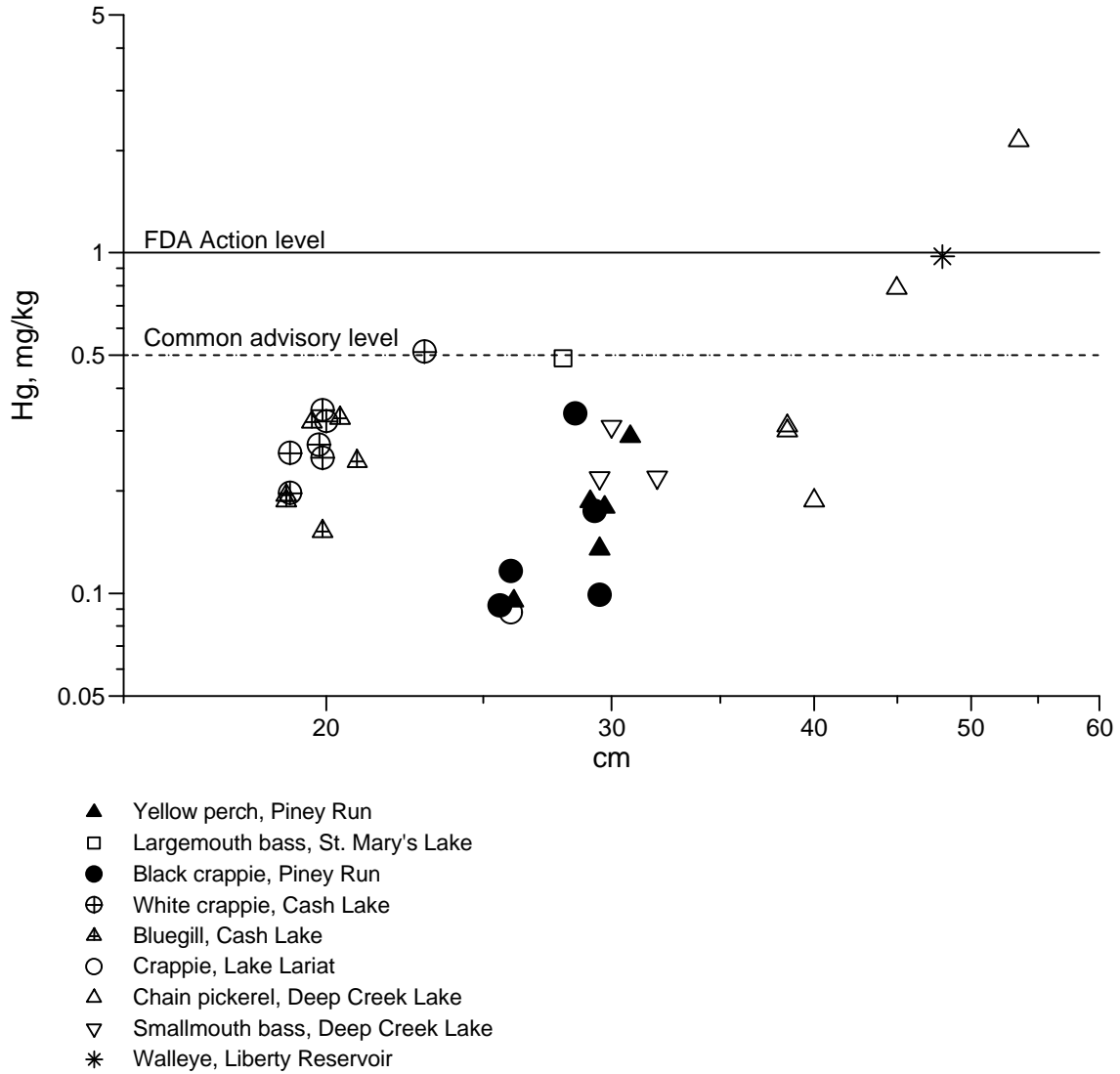
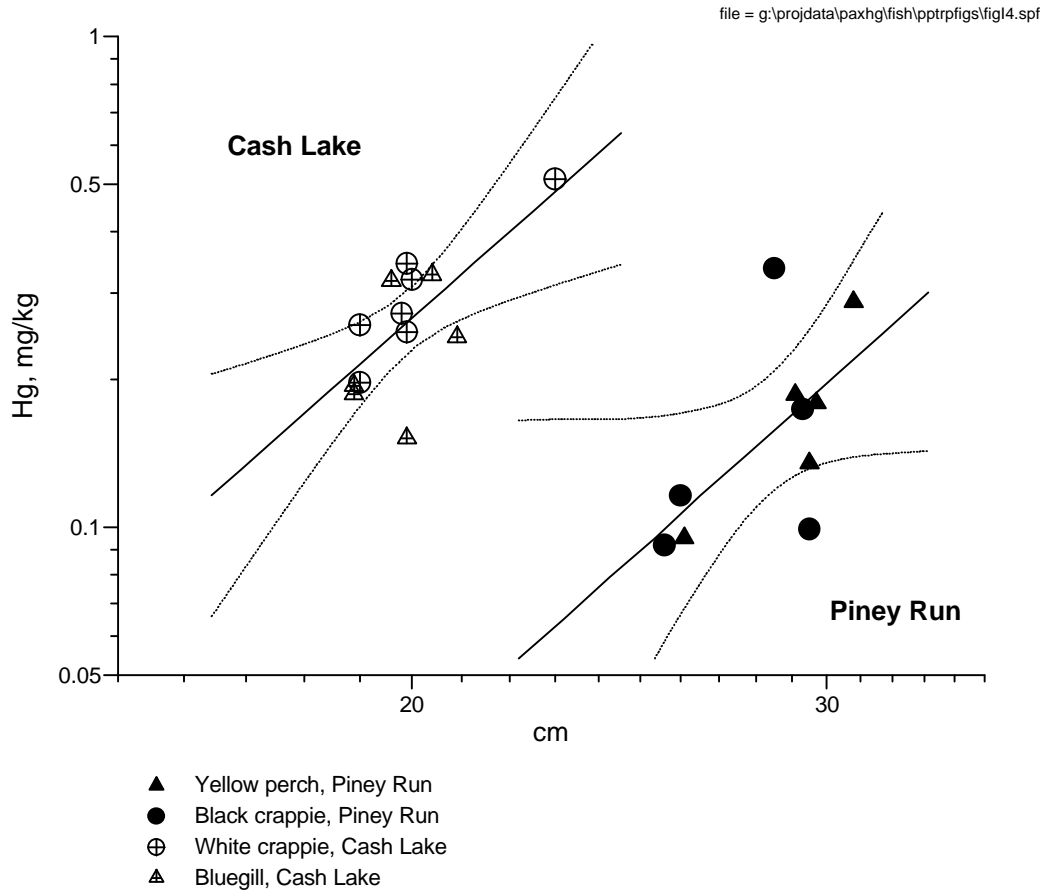


Figure 6. Relationship between ln Hg concentration (mg/kg) and ln length (cm) for all freshwater sportfish (except striped bass) examined.



Figure

e 7. Comparison of Hg levels in pan fish between two lakes, Cash Lake and Piney Run.

Table 12. Regression analysis of freshwater fish by length					
Site	Species	P	r ²	n	regression equation
Cash Lake	White crappie	<0.006	0.81	7	ln Hg = (4.2 X ln cm) - 13.9
	White crappie and bluegill	<0.008	0.49	13	ln Hg = (4.2 X ln cm) - 14
Piney Run	Yellow perch	<0.05	0.79	5	ln Hg = (5.8 X ln cm) - 21.3
	Yellow perch and black crappie	<0.057	0.38	10	ln Hg = (4.3 X ln cm) - 16.2
Deep Creek L.	Chain pickerel	<0.01	0.90	5	ln Hg = (6.5 X ln cm) - 25.2

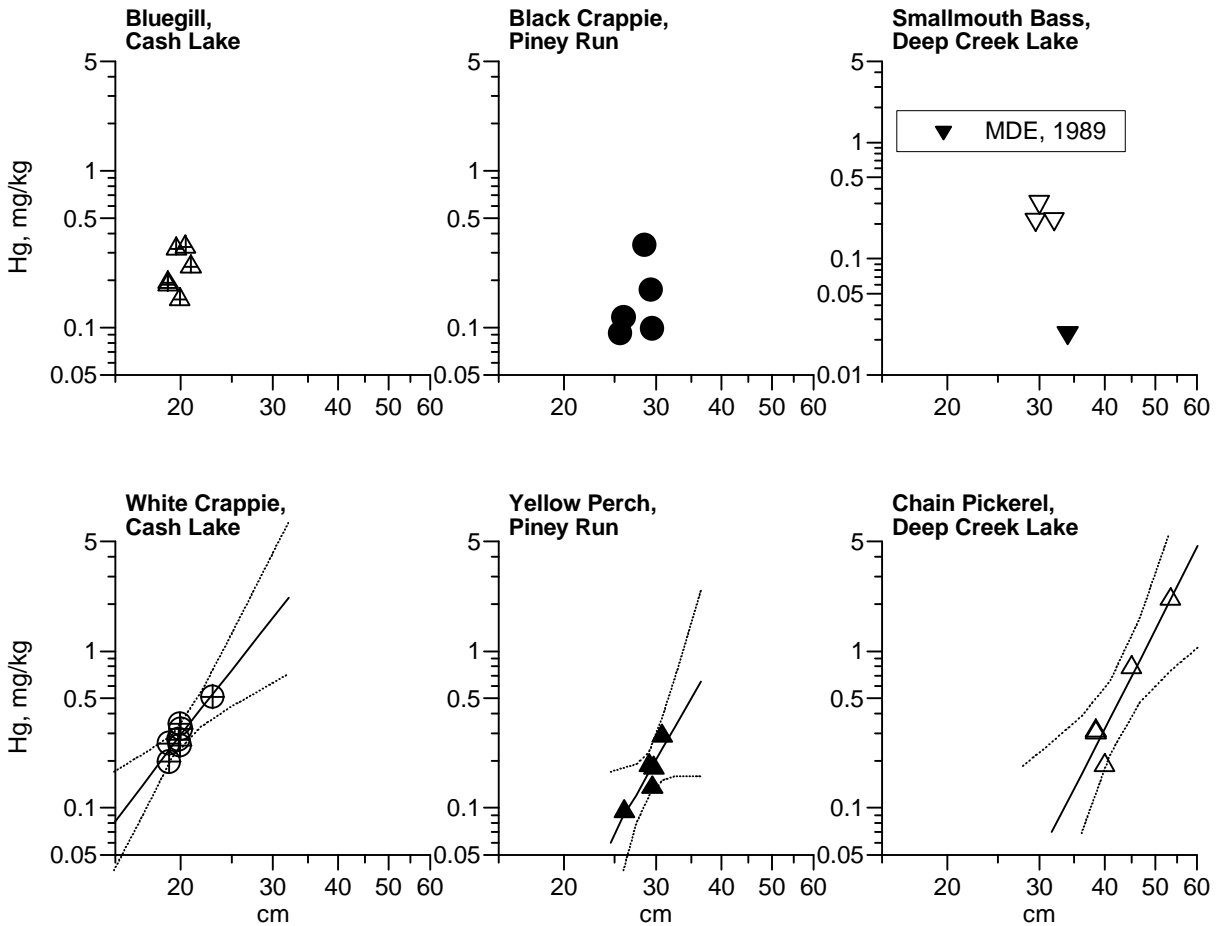


Figure 8. Individual relationships between ln Hg concentration (mg/kg) and ln length (cm) for each freshwater species examined except striped bass. Solid lines are linear regressions of each data set where $P < \text{about } 0.1$; equations for the regressions are given in each panel along with P and r^2 values for each. Dotted lines represent 95% confidence intervals around the mean. Note the different scale for largemouth bass.

and length (Fig. 8) for the Cash Lake white crappie were significant. These regressions suggest that crappie over 0.17 kg or 23 cm will exceed 0.5 mg/kg; and fish over 0.3 kg or 30 cm will exceed 1 mg/kg. Crappie examined from Piney Run were 6-10 cm longer than crappie with the same Hg concentration in Cash Lake. The relatively high levels of Hg in pan fish give a warning that any higher level piscivores in the lake should be examined. If there is a sports or subsistence fishery in Cash Lake, Hg in fish should be examined in more detail, in both pan fish and in any larger sportfish.

Mercury levels in fish from Piney Run appear intermediate in Hg content in comparison with other water bodies in Maryland, and throughout the U.S. and Canada. Mercury levels in Piney Run perch were higher than yellow perch taken from Chesapeake Bay, but lower than fish taken from lakes in other states where consumption advisories are posted for top piscivores. Regression of the Piney Run yellow perch data on Hg concentration was also significant, and suggests that fish over 39 cm would exceed 0.5. Yellow perch analyzed from Piney Run and from the Patuxent River were about the same size (about 30 g), but freshwater Piney Run yellow perch contained 0.15-0.3 mg Hg/kg, while the estuarine Patuxent fish contained 0.1-0.18 mg/kg. For comparison, Hg levels in similar size yellow perch in a few other U.S. fresh waters are listed below. Many of the Maine and Michigan lakes included in the surveys in Table 13 are influenced by either low pH or high DOC, water quality factors that favor MeHg production and bioaccumulation.

Table 13. Comparison of Hg concentrations in yellow perch among selected North American lakes.			
Location	Mean length, cm	Mean Hg, mg/kg	Citation
Piney Run Res, MD	29	0.18	This report
Maine lakes	23	0.28	Stafford and Haines 1997
Michigan UP lakes (seepage)	30	0.35	Grieb et al. 1990
Michigan UP lakes (drainage)	30	1.0	Grieb et al. 1990

Liberty Reservoir. The one walleye examined from Liberty Reservoir was 48 cm long and contained 0.98 mg Hg/kg (Fig. 6). This value is at the upper end of the distribution of Hg concentrations in similar size walleye from Wisconsin lakes (Wiener et al. 1990b) and Ontario lakes (Ontario Ministry of the Environment 1988), both areas with generally high Hg levels in fish. OME estimates that the “natural” Hg level for 50 cm walleye is about 0.2 mg/kg, based on levels in the least contaminated Great Lakes. As discussed above, large striped bass from Liberty were also high in Hg, and exceeded the FDA action level (Fig. 1).

Deep Creek Lake pickerel. Large chain pickerel in Deep Creek Lake exceed the FDA action level (Fig. 6). The ANSERC data reported here suggest that Hg concentrations in chain pickerel in Deep Creek Lake are quite high. Collection of enough fish over a sufficient size range gave a significant regression for Hg against both weight and length (Fig 9, Table 14). Using this analysis, pickerel over 0.5 kg exceed 0.5 mg Hg/kg and over 0.7 kg exceed 1 mg Hg /kg. Versar examined walleye and chain pickerel in 4 of the larger Maryland reservoirs in 1992 (Versar 1994). Fish mercury data from that 1994 PPRP report are plotted by length in Fig. 9, for comparison with data in this study. Regression of the combined ANSERC and Versar data sets (Figure 4) suggests that pickerel over 44 cm would exceed 0.5 mg Hg/kg and over 48cm would exceed 1 mg Hg /kg. Of the species and lakes examined, only chain pickerel in Deep Creek Lake were examined in both studies. The ANSERC and Versar data sets are complimentary, with the Versar data strengthening confidence that large pickerel in this lake exceed the FDA action level. ANSERC and Versar data for Hg in Deep Creek Lake chain pickerel are plotted together in Fig. 10, and regression analysis for the combined data sets given in Table 14. Versar measured lower Hg concentrations in Herrington Manor Lake chain pickerel than in smaller pickerel from Deep Creek Lake (Fig. 9). The size range of the fish sampled by Versar in both studies was too narrow to give significant size:Hg regressions.

Mercury values for Deep Creek pickerel can also be compared with an ANS data set collected for chain pickerel from a large number of New Jersey lakes (Horwitz et al. 1994, 1995). Many lakes in New Jersey contain fish with elevated Hg concentrations. Because of the large number of affected lakes, consumption advisories for fish were put in place for all New Jersey lakes in 1994. Low pH, high DOC lakes in the New Jersey Pine Barrens in particular contain pickerel with very elevated levels of Hg. Pickerel from Deep Creek contained Hg concentrations at the upper end of the range found in New Jersey pickerel of the same size, comparable to pickerel in Pine Barrens Lakes.

Walleye in Deep Creek and other reservoirs. Two of the five walleye sampled in Deep Creek by Versar in 1992 contained >0.5 mg Hg/kg, with one 42 cm fish containing 0.93 mg Hg/kg (Fig. 9). Of the data collected on reservoir walleye by Versar, only the walleye collected in Jennings Randolph Reservoir produced a significant size:Hg regression (Fig 9). Although only 3 fish were examined, it appears that even very large walleye in Jennings Randolph Reservoir (70 cm) would not exceed consumption advisory levels. Walleye from Deep Creek Lake and Savage Reservoir appear to contain more Hg per unit weight than walleye from Jennings Randolph Reservoir, as concluded in the 1994 Versar report.

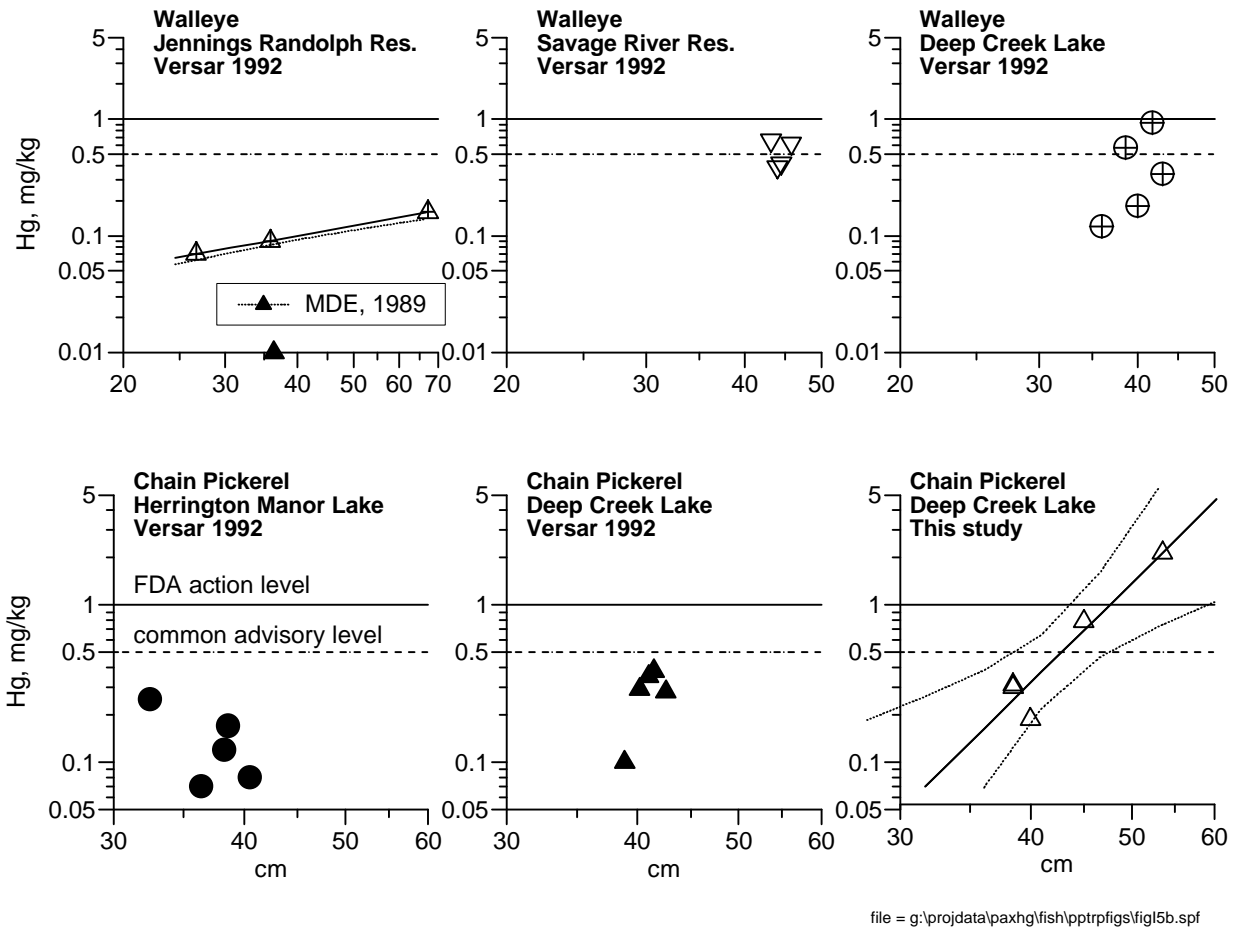


Figure 9. Individual relationships between ln Hg concentration (mg/kg) and ln length (cm) for walleye and chain pickerel in reservoirs. Data from Versar, MDE and this study as noted. Solid lines are for significant linear regressions; equations for the regressions are given below. Dotted lines represent 95% confidence intervals around the mean.

Table 14. Regression analysis of chain pickerel by length						
Site	Study	Species	P	r ²	n	regression equation
Deep Creek L.	ANSERC	Chain pickerel	<0.01	0.90	5	ln Hg = (6.5 X ln cm) - 25.2
Deep Creek L.	ANSERC + Versar	Chain pickerel	<0.01	0.78	10	ln Hg = (7.3 X ln cm) - 28.2
Jennings Randolph	Versar	Chain pickerel	<0.01	0.99	3	ln Hg = (0.9 X ln cm) - 5.6

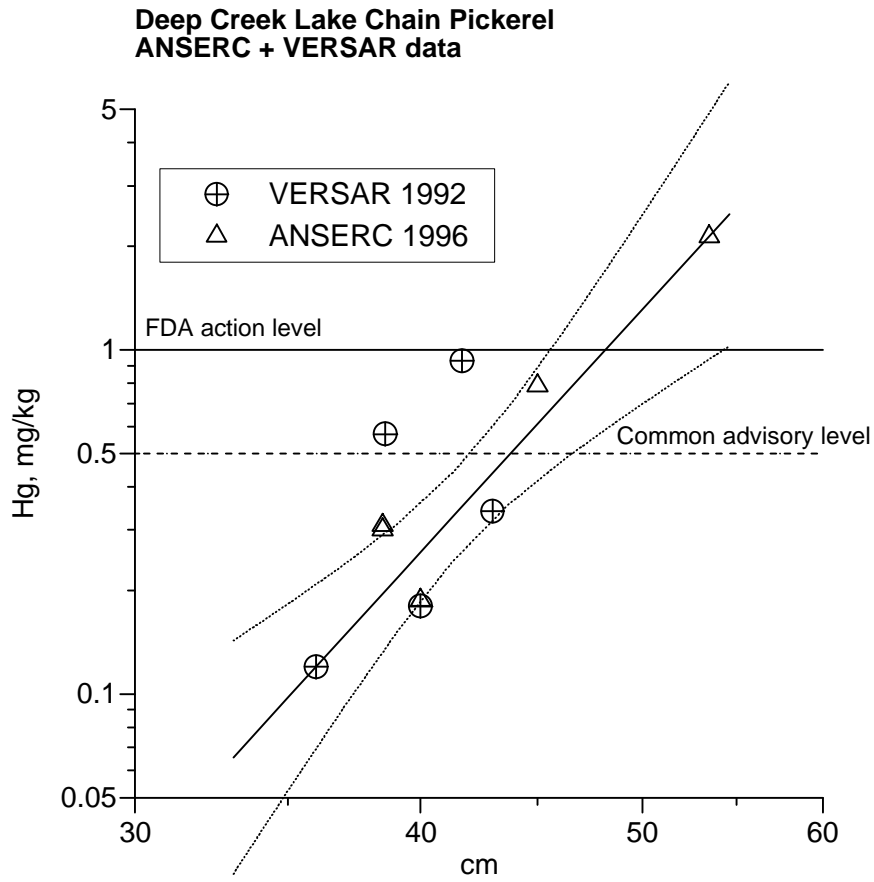


Figure 10. Comparison of ANSERC and Versar data on Hg in chain pickerel in Deep Creek Lake. The solid line represents the linear regression of both data sets; regression data are given in Table 14. Dotted lines represent 95% confidence intervals around the mean.

MDE examined Hg in reservoir fish in 1989 (Versar 1994). Mercury concentrations were averaged for fish of different sizes. Where direct comparisons can be made, the Hg concentrations measured by MDE were about ten times lower than concentrations measured in similar size fish by Versar or ANSERC. MDE data for smallmouth bass in Deep Creek Lake and walleye in Jennings Randolph Reservoir are plotted for comparison in Figs. 8 and 9.

Bass in Deep Creek and St. Mary's Lakes. Smallmouth bass averaging 30 cm from Deep Creek Lake contained about 0.3 mg Hg/kg, but no larger bass were examined (Fig 6). Mercury in one largemouth bass collected from St. Mary's Lake in southern Maryland was somewhat higher (0.49 mg/kg) at roughly the same size. Table 15 lists Hg concentrations in largemouth and smallmouth bass measured in this study, including Hg values for the smallest size class of tidal largemouth bass. These values are compared with data on comparable size bass from lakes in other regions. Many of the lakes for which data are given are affected by acid deposition, depressed pH or high DOC. Bass from both St. Mary's and Deep Creek showed similar size to Hg ratios as bass in other lakes where consumption advisories are posted, while bass from the Patuxent and Potomac rivers contained less Hg at larger sizes. St. Mary's Lake is a poorly buffered, high DOC lake. Deep Creek Lake is also poorly buffered, and is affected by acid precipitation and acid mine drainage. A more careful examination of bass from both Deep Creek and St. Mary's Lake should be considered. Both lakes have substantial recreational fisheries.

Table 15. Comparison of Hg concentrations in like-sized largemouth (LM) and smallmouth (SM) bass among North American lakes.

Location	LM or SM	n	Mean length, cm	Mean Hg, mg/kg	Citation
Potomac River, MD	LM	9	44	0.16	This report
Patuxent River, MD	LM	2	42	0.18	This report
Deep Creek Lake, MD	SM	3	31	0.25	This report
Lake Tohopekaliga, FL	LM	many	30	0.27	Lange et al. 1994
St. Mary's Lake, MD	LM	1	28	0.49	This report
Ontario Lakes	LM	14	30	0.46	Wiener and Spry 1996
Ontario Lakes	SM	72	30	0.53	Wiener and Spry 1996
Maine Lakes	LM	15	31	0.56	Stafford and Haines 1997
Maine Lakes	SM	56	32	0.66	Stafford and Haines 1997
Florida Lakes	LM	25	36	0.76	Lange et al. 1993

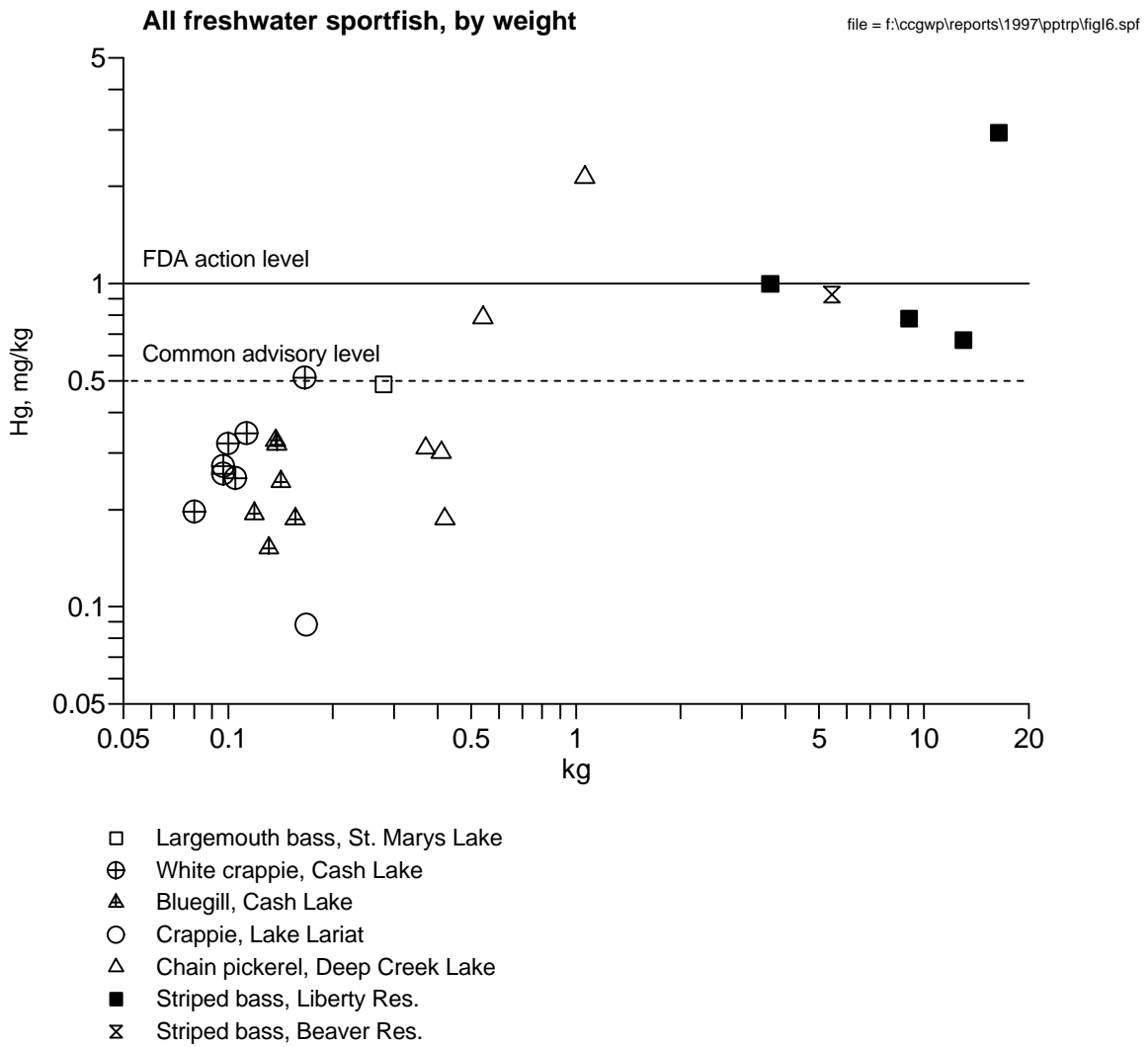
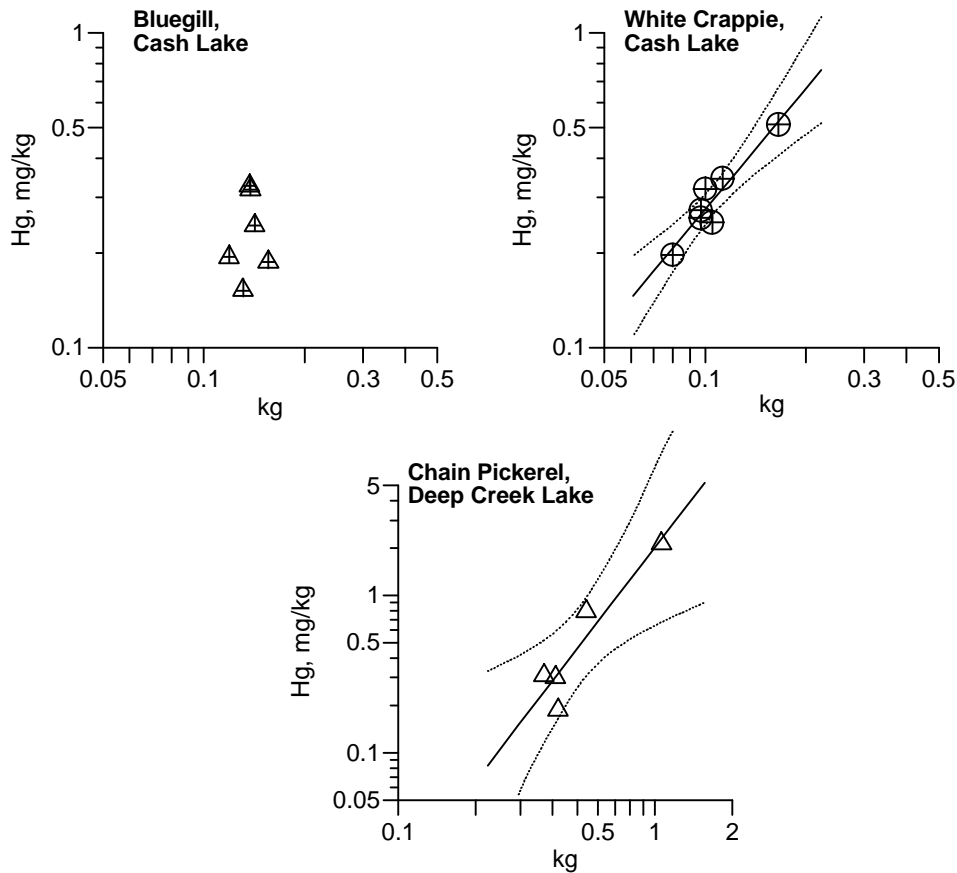


Figure 11. Relationship between ln Hg concentration (mg/kg) and ln weight (kg) for all freshwater sportfish for which weight was available.



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Figure 12. Individual relationships between ln Hg concentration (mg/kg) and ln weight (kg) for freshwater species for which weight was available. Solid lines are linear regressions of each data set where $P < \text{about } 0.1$; equations for the regressions are given below in Table 16. Dotted lines represent 95% confidence intervals around the mean.

Table 16. Regression analysis of freshwater fish by weight					
Site	Species	P	r^2	n	regression equation
Cash Lake	White crappie	<0.01	0.90	7	$\ln \text{Hg} = (-1.64 \times \ln \text{kg}) + 1.27$
Deep Creek L.	Chain pickerel	<0.02	0.87	5	$\ln \text{Hg} = (-0.7 \times \ln \text{kg}) + 2.13$

Modeling MeHg bioaccumulation

The state of Maryland has evaluated the use of mathematical models to predict MeHg bioaccumulation among ecosystems (Logan 1998). The Electric Power Research Institute has funded development of the Mercury Cycling Model (MCM) over the last decade (e.g. Hudson et al. 1994). The model incorporates the full spectrum of known biogeochemical and bioaccumulative reactions involving Hg. It is the most sophisticated model available for aquatic Hg cycling, and reflects state of the art understanding of research developments in this field.

Effective and efficient regulation of Hg emissions requires the ability to predict the amount of reduction of MeHg in fish for a given reduction in Hg emission. A number of factors contribute to current uncertainty in those predictions, but one of the largest sources of uncertainty is in the production of MeHg. Increased deposition of mercury from the atmosphere to watersheds is translated into human and wildlife health risks only after methylation and subsequent bioaccumulation in fish.

The variability in MeHg production and accumulation among ecosystems is as large or larger than the range in atmospheric Hg deposition rates across the U.S. (about 3 orders of magnitude; Heyes and Gilmour 1999). Biogeochemical factors that affect Hg bioavailability in sediments and the activity of Hg-methylating microorganisms influence methylation rates and contribute to variability in MeHg among ecosystems. Of these biogeochemical factors, sulfur appears to be particularly important. Methylation/demethylation is not currently well parameterized in MCM. This reflects the state of scientific knowledge rather than a gap in the model. Watershed morphology also contributes to variability, because Hg methylation is a microbial process that occurs predominantly in wetlands, aquatic sediments, and temporally saturated soils (St. Louis et al. 1994, 1995; Krabbenhoft et al. 1995; Branfireun et al. 1996). Therefore, the percent wetlands in catchments (St. Louis et al. 1995; Driscoll et al. 1994), and the percent littoral area in lakes (Bodaly et al. 1993) affect MeHg production.

The variability in the Hg to MeHg relationship among ecosystems is high and not fully understood. As a result, MCM is not currently capable of predicting net MeHg production among ecosystems. Among systems where MeHg production would be expected to vary widely, MCM should not be used at this time to predict MeHg concentrations in fish, or to predict how management strategies would affect MeHg production. However, MCM will become a more valuable tool for predictions among lakes as efforts to model methylation rates progress in the next few years. Efforts to improve methylation/demethylation modeling in MCM are underway, using the Florida Everglades as a primary model ecosystem. Among others, we are working with Reed Harris of Tetra Tech to identify the reaction parameters that best predict MeHg accumulation in sediments and water. Research on the control of MeHg production among ecosystems is needed to allow models like MCM to have predictive value for managers.

In their analysis of MCM model use in Maryland, Logan et al. concluded that fish Hg concentrations among lakes are relatively insensitive to changes in net methylation rate. This conclusion was based on a model sensitivity analysis done using 20% changes in most

parameters. However, factors of up to three orders of magnitude difference in net methylation among lakes should be expected, and model sensitivity should be examined over this range of methylation rates. Further, Logan et al. used MDE and Versar data for walleye from Jennings Randolph in model sensitivity testing. Difficulties in assessing the ability of the MCM model to predict Hg in Maryland fish may have arisen in part from the large discrepancy between the MDE and Versar data.

Currently, a jurisdiction wishing to identify aquatic ecosystems most at risk for Hg bioaccumulation, or to design a water body Hg screening program, is best served by using the professional best judgement of experts in the field rather than mathematical models. This is the basic approach ANS used in choosing lakes types for sampling during our study of Hg in New Jersey fish. Aquatic ecosystems at risk for high Hg in fish are mainly fresh waters with low pH and/or high DOC (color); newer reservoirs; lakes with anoxic hypolimnia; lakes with large wetland areas in their watersheds, and lakes directly contaminated by point sources of Hg. A number of water bodies in Maryland have one or more of these characteristics, and it would be surprising if fish from these waters did not contain elevated Hg concentrations. Fresh waters impacted by high levels of atmospheric Hg deposition, like most Maryland waters, are particularly at risk. A few notable coastal ecosystems also contain contaminated fish, e.g. south Florida coastal waters. Almost every state has reason to measure Hg levels in fish from some or all water bodies, and most states have issued resultant advisories.

SUMMARY

The experiences of other U.S. states and other countries strongly suggest that certain types of water bodies in the state of Maryland will contain fish that exceed common advisory levels for Hg. The limited data set presented here supports that notion. These data suggest that there is particular reason for concern about Hg in chain pickerel, largemouth bass, smallmouth bass and larger striped bass, in Maryland lakes and reservoirs, while Hg in Chesapeake Bay striped bass should be of much less concern. This work indicates that a more comprehensive study of Hg in Maryland fish is warranted.

In Maryland, as expected, freshwater fish contained proportionally more Hg at the same size than did fish from Chesapeake Bay. Of the fish examined, the largest freshwater sportfish contained the highest levels of Hg. Large piscivores from Deep Creek Lake and Liberty Reservoir exceeded the FDA action level of 1 mg Hg/kg fish tissue. Fish in Beaver Run and Cash Lake exceeded 0.5 mg Hg/kg fish tissue, a tissue screening level used by many states in issuing human consumption advisories. For most fish species in most lakes, Hg concentrations increased with the size of fish. Weight was a better predictor of Hg concentration than fish length. Mercury bioaccumulation in fish varied among freshwater bodies, as measured by differences in the Hg to weight relationships among lakes.

Large striped bass taken from Liberty and Beaver reservoirs contained Hg that exceeded common advisory levels, and had more Hg at the same size than did Chesapeake Bay striped bass.

However, the number of reservoir striped bass sampled in this survey was very small. The larger data set collected for estuarine striped bass suggests that only very large rockfish in the Chesapeake Bay contain Hg at levels that are above common advisory levels. Fish in the upper reaches of rivers and the upper Bay appear to contain slightly more Hg at the same weight than do fish caught in the central mainstem. However, the difference between striped bass from reservoirs and the Bay is much more pronounced. A more complete analysis of Hg in striped bass from Maryland reservoirs, at least, is certainly needed. No other large game fish from Chesapeake Bay were examined in this study.

In Deep Creek Lake, Hg concentrations in chain pickerel appeared quite elevated. Enough pickerel were collected to provide a good relationship between length and Hg concentration, increasing confidence that these fish are representative of the system. Data collected as part of this study were similar to Hg concentrations measured in Deep Creek pickerel by Versar in 1992. However, MDE has reported much lower values for Hg in reservoir fish than those reported by ANSERC and Versar. Mercury concentrations in smallmouth bass from Deep Creek may also be somewhat elevated. Deep Creek Lake has many characteristics that make it a candidate for elevated MeHg production and bioaccumulation (acid deposition and acid mine drainage; high atmospheric Hg deposition; reservoir), and it is a heavily used recreational fishery. Deep Creek Lake should become a focus of state monitoring efforts for Hg in fish.

Panfish were examined in two impoundments, Cash Lake in Prince Georges County and Piney Run Reservoir in Carroll County. Crappie from Piney Run were 6-10 cm longer than crappie with the same Hg concentration in Cash Lake. Large differences in size-normalized Hg concentrations between the lakes highlight the large differences in MeHg production and bioaccumulation among ecosystems. The largest white crappie analyzed from Cash Lake (23 cm) contained more than 0.5 mg Hg/kg. High Hg levels in panfish in Cash Lake suggest that fish in this lake should be examined in more detail, particularly if the lake supports higher trophic level species.

A variety of fish from the tidal freshwater and oligohaline Patuxent and Potomac were examined. Of the species examined (largemouth bass, yellow perch, catfish, white perch and croaker), only extremely large largemouth bass (> 4 kg) would be expected to exceed 0.5 mg/kg. Catfish contained the least Hg for their size. This is often the case with omnivorous fish, who may eat lower on the food chain than piscivores of the same size. Largemouth bass and yellow perch taken from these tidal rivers contained less Hg than did the same species taken from Maryland fresh waters impoundments.

Elevated levels of Hg in fish are a potential threat to wildlife as well as to human health. Decreased reproductive success is probably the most important route of MeHg toxicity in fish, birds and mammals. Wiener and Spry (1996) report decreased hatching success and embryo survival in eggs from walleye containing less than 0.6 mg MeHg/kg in maternal muscle. Wading birds and piscivorous mammals are most likely to accumulate the highest tissue concentrations of MeHg (U.S. EPA 1997).

The results of this survey are not meant to be a statistically rigorous assessment of Hg levels in Maryland fish, nor does this study provide sufficient information to make decisions about consumption advisories. These data add to the State of Maryland's general survey of contaminants in fish composites by providing size-specific data for Hg in fish, and by providing data on fish in fresh waters, many of which have not been included in the state survey. Although these data are limited, they provide a warning that large fish from some Maryland fresh waters exceed recommended limits for human consumption.

Further assessment of Hg levels in Maryland sportfish is needed to protect human and wildlife health. The most important changes to the current State of Maryland fish contaminant sampling strategy should be: 1) an increased sampling intensity in fresh waters that have characteristics putting them at risk for Hg bioaccumulation, 2) targeted sampling of piscivores, 3) size-stratification of fish sampling into three to five relatively narrow size classes and 4) rigorous quality assurance of Hg analytical data including interlaboratory calibrations.

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