Methylmercury Concentrations in Fish from Tidal Waters of The Chesapeake Bay

Robert P. Mason,[1,2] Deborah Heyes,[1] Auja Sveinsdottir[1]

[1] Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science, One Williams Street, P.O. Box 38, Solomons, Maryland 20688, USA

[2] Department of Marine Sciences, University of Connecticut, Groton, CT 06340, USA

Abstract. Striped bass (*Morone saxatilis*), white perch (*Morone americana*), and largemouth bass (*Micropterus salmoides*) were collected in the Chesapeake Bay mainstem and tributaries and analyzed for total mercury (Hg) and methylmercury (MeHg) content. Striped bass are anadromous, whereas white perch and largemouth bass are resident species, and the largemouth bass are also restricted to the tidal fresh portion of the Bay. Total Hg and MeHg concentrations in striped bass increased with fish size, and large fish (>7.5 kg wet weight) tended to have MeHg concentrations of 300 ng g^{-1} or greater. On average, the striped bass MeHg concentration was 120 ± 100 ng g^{-1} and the fraction of the total Hg as MeHg was 65 ± 22%. Reasons for the lower relative MeHg content are discussed. Otolith strontium/calcium ratios were also determined to examine whether migration had a significant impact on MeHg content in striped bass. Resident fish did appear to have a higher MeHg burden than the more migratory fish of similar size. Largemouth bass and white perch tended to have low MeHg content (respectively, 14 ± 7 and 13 ± 11 ng g^{-1}; all fish <1 kg wet weight), and the white perch also had a low %MeHg (28 ± 14%), reflecting their mostly planktivorous lifestyle. A comparison of largemouth bass and striped bass MeHg concentrations for the estuarine fish with those of fish in Maryland reservoirs of similar size showed that the estuarine fish have much lower MeHg burdens. Differences in MeHg concentration in the estuarine waters compared to the reservoir waters likely account for much of this difference, although the importance of other factors is also discussed.

Heightened concerns for human and ecosystem health have led to increased study of mercury (Hg) in the environment. Accumulation of methylmercury (MeHg) by fish is the primary concern, because consumption of MeHg-contaminated fish is the major route for transfer of MeHg from the aquatic environment to fish-eating birds and mammals, including humans (Rodgers 1994; Wolfe *et al.* 1998; Fitzgerald and Clarkson 1991; Weiner *et al.* 2002). Prenatal life and small children are more susceptible to brain damage because of their enhanced sensitivity to the neurotoxin (Weiss *et al.* 1999). Public health warnings and guidelines for consumption of fish with elevated levels of MeHg have been issued by the World Health Organization (WHO 1990), in parts of Scandinavia and Canada, by the U.S. Food and Drug Administration (USFDA 2002), the U.S. Environmental Protection Agency (USEPA 1995), and numerous other agencies and governments. In March 2001, USEPA and USFDA posted a consumer advisory about the risk of MeHg in fish, advising pregnant women, women of childbearing age who may become pregnant, and young children not to eat piscivorous fish that accumulate the highest levels of MeHg (USFDA 2002). In December 2001, Maryland (MD) released an advisory based on preliminary results from studies in MD reservoirs (Mason and Sveinsdottir 2003; Sveinsdottir and Mason 2005; Gilmour and Reidel 2000; MDE 2004). Preliminary data on tissue concentrations for Chesapeake Bay fish indicated lower levels than found in the reservoirs of MD for fish occupying similar trophic levels (Gilmour 1999). Given that other coastal environments have elevated fish Hg concentrations, and that some states have issued advisories for coastal waters (USEPA 2004), this study was initiated to examine the concentration of MeHg in estuarine fish in the Chesapeake Bay and the factors influencing their concentration.

Mercury occurs in the environment in a variety of inorganic and organic compounds, not only in solid or dissolved states, but also in liquid and gas phases (Mason and Benoit 2003; Morel *et al.* 1998). Although Hg is mostly emitted to the atmosphere in the form of inorganic Hg—elemental (Hg^0) and ionic Hg^{II}—the majority of the Hg in fish is MeHg. It is more toxic and bioaccumulative and has a large capacity for biomagnification in food webs, mostly through food consumption (Rodgers 1994; Hudson *et al.* 1994). Atmospheric deposition of Hg is the dominant source to freshwater and marine systems (Mason *et al.* 1994; Rolfhus and Fitzgerald 1995), and the sources of Hg to the atmosphere are both natural and anthropogenic (Mason *et al.* 1994; Mason and Sheu 2002), with anthropogenic inputs currently exceeding natural input by at least twofold. Highest levels of deposition are in developed locations and around point sources, as we have demonstrated for Maryland (Mason *et al.* 1997; Mason *et al.* 2000; Sheu *et al.* 2002). Population growth and urbanization have

Correspondence to: Robert P. Mason; *email:* robert.mason@uconn.edu

contributed to significantly elevated levels of Hg in sediment, water, and the atmosphere in the Mid-Atlantic United States (Mason *et al.* 1999; Mason and Lawrence 1999). However, the impact of these elevated levels on the concentrations of MeHg in fish in the mainstem Chesapeake Bay has not been adequately examined. The current study was designed to address this issue.

Sources of MeHg to aquatic systems are from precipitation, typically a minor source, from *in situ* methylation and from runoff from wetlands and the watershed (Watras *et al.* 1994; Rudd 1995). For the Chesapeake Bay, Mason *et al.* (1999) estimated that more than 60% of the MeHg in the Chesapeake Bay system is derived from *in situ* methylation. It has been estimated that sediment is an important sink for Hg but a likely source for MeHg in the Chesapeake Bay (Benoit *et al.* 1998; Mason *et al.* 1999; Mason and Lawrence 1999). Mercury is converted to MeHg via *in situ* methylation by sulfate-reducing bacteria in anoxic sediments (Gilmour *et al.* 1992; Benoit *et al.* 2003). Overall, MeHg bioaccumulation in fish not only depends on how much Hg enters the ecosystem, but also on the ability of an ecosystem to convert Hg to MeHg (Benoit *et al.* 2003). Although the elevated sulfate concentrations in estuaries may enhance sulfate reduction, buildup of sulfide may limit methylation (Benoit *et al.* 1999, 2001; Heyes *et al.* 2006). Highly contaminated environments, such as Baltimore Harbor, may not have as elevated MeHg in fish because of nonlinearities between total Hg input, MeHg formation, and MeHg bioaccumulation (Heyes *et al.* 2004, 2006; Benoit *et al.* 2003), and between MeHg concentration in water and sediment and MeHg in biota, especially benthic organisms (Lawrence *et al.* 1999; Lawrence and Mason 2001; Mason and Lawrence 1999). This is because 1) highly contaminated and generally eutrophic systems have higher sulfide levels in sediments, and sulfide has been shown to inhibit Hg methylation (Benoit *et al.* 2003); and 2) the bioavailability of MeHg to bioaccumulation in food chains appears to be a function of organic content, with lower relative accumulation from media (sediment or water) with higher organic content (Mason 2002). Thus, both of these factors lead to a relatively lower accumulation of MeHg into fish in more eutrophic and contaminated systems.

Once MeHg enters the food chain, it is efficiently accumulated and transferred to organisms at higher trophic levels (Mason 2002). The burden of MeHg in fish depends on many physicochemical variables, but water chemistry is likely to be an important factor controlling bioaccumulation rate, especially in pelagic-dominated food chains. Various variables, including Hg and MeHg concentration, water temperature, dissolved oxygen (DO), dissolved organic carbon (DOC), pH, total suspended solids (TSS), particulate organic carbon (POC), and sulfate concentrations, have been shown to influence both methylation of Hg and the uptake and accumulation of MeHg by fish from sediment and the water column (Hudson *et al.* 1994; Driscoll *et al.* 1995; Benoit *et al.* 2003; Mason and Benoit 2003; Sveinsdottir and Mason 2005).

Three fish species were chosen for the current study based on their different life histories. Striped bass (*Morone saxatilis*) are found in shallow coastal waters and migrate in and out of the estuaries, especially as they get older (Mansueti 1961). To determine the extent to which the striped bass in the Chesapeake Bay were resident species, otoliths were collected for analysis from fish, where possible, and were analyzed for their
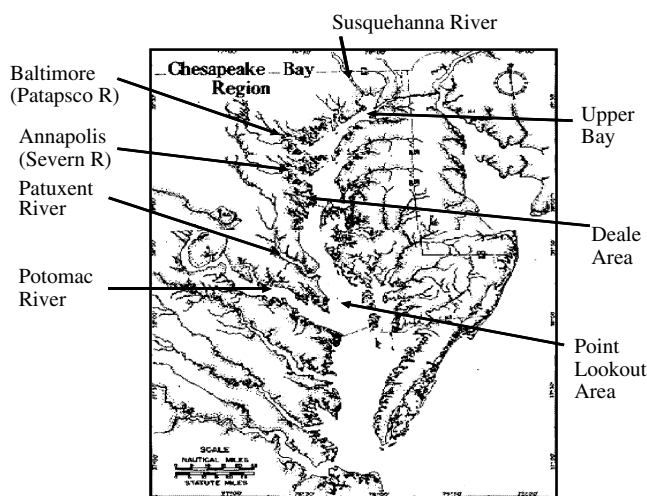

Fig. 1. Map of the Chesapeake Bay showing the sampling site locations.

strontium (Sr) to calcium (Ca) ratio. Otolith relative concentrations are related to the water the fish reside in. Ocean water Sr:Ca molar ratios are between 8.5 and 9 mmol mol^{-1}, and freshwater values tend to be much less (typically < 5), although they can be highly variable (Kraus and Secor 2004). The Sr:Ca ratio therefore gives an indication of the life history of the fish. Although it is possible to analyze the otoliths in detail to obtain yearly information on migration patterns (*e.g.,* Secor *et al.* 2001), analysis of the whole otolith provides an indication of general life history.

In addition to striped bass, white perch (*Morone americana*) and largemouth bass (*Micropterus salmoides*) were also analyzed. White perch are typically resident within subestuaries because they mostly inhabit relatively low-salinity waters. Largemouth bass are only found in the tidal fresh reaches of the Chesapeake Bay. It was hypothesized that the estuarine fish would have lower concentrations than those in freshwater, for fish of similar size and trophic level. This hypothesis was based on the knowledge that MeHg concentrations in Chesapeake Bay waters are lower than in the freshwater reservoirs (Mason *et al.* 1999; Sveinsdottir and Mason 2005), and on studies in the reservoirs that suggested that dissolved MeHg was the most important controlling factor for fish MeHg concentration. Furthermore, this study was designed, through the use of otolith analysis, to ascertain the importance of migration on influencing striped bass MeHg concentration.

Materials and Methods

Fish were collected by various methods and at various locations in the Chesapeake Bay and its tributaries. In fall 2002, striped bass were collected by Maryland Department of Natural Resources (MD DNR) personnel at two locations in the Chesapeake Bay (Figure 1): 1) off Point Lookout, which is at the mouth of the Potomac River, and is therefore representative of the mid to lower portion of the Chesapeake Bay; and 2) off Deale, which is representative of the mid-bay region. These fish were collected using pound nets and were generally of smaller size, between 1 and 2 kg. In addition, striped bass were caught in spring 2003 and summer 2004 by individual anglers and samples

were provided to Chesapeake Biological Laboratory (CBL) for analysis. These fish were caught from the mid-to upper bay (mouth of the Potomac to the mouth of the Susquehanna). Fish were caught during the spring migration in 2003 in an effort to obtain large, and probably migratory, fish and were caught using typical angling techniques (rod + reel). To further enhance the dataset, additional samples were provided by the same fishermen of fish caught during the summer of 2004. It was not possible to ascertain the exact location of capture in each case, but as striped bass move widely throughout the Bay and also migrate offshore, the location of capture is not likely representative of the location where the fish typically resides.

Also in fall 2002, largemouth bass were collected from the tidal reaches of the upper Chesapeake Bay and its tributaries by MD DNR personnel by electroshocking. This technique does not typically sample the larger fish, and the fish obtained were less than 1 kg. Locations included the upper bay and near the mouth of the Susquehanna River (Figure 1). In spring 2003, white perch were collected from the Choptank River, which flows into the mainstem mid-bay, and the Severn River, near Annapolis, using nets. Other white perch were obtained from Maryland Department of Environment (MDE), collected as part of their routine fish monitoring program (MDE 2004). These fish were from the Patapsco River, rivers on the upper and lower eastern shores, from the South River near Annapolis, and from the Potomac and Patuxent River (Figure 1).

In the field, all fish were handled by gloved personnel, and after rinsing and measurement, each fish was bagged in a plastic Ziploc bag. The fish were kept cold (on ice), with each bagged fish wrapped in aluminum foil and then bagged in a second Ziploc bag. Fish were shipped overnight to the CBL on ice, or were picked up in the field by CBL personnel. For the striped bass caught by line, the fish were filleted in the field and a portion of the muscle tissue closest to the head was bagged and frozen until delivery to CBL. At CBL, the weight and length of each fish were measured if this had not already been done. Fish were filleted and muscle tissue from both sides of each individual fish (representing the portion of fish normally consumed by humans) was removed and homogenized in a blender in a noncontaminating environment and then stored frozen in a Ziploc bag until further analysis. All sampling equipment, such as stainless steel knives and food processors, were acid cleaned prior to use and in between fish. In addition, otoliths were removed and washed in distilled water and stored for analysis, when possible.

For MeHg analysis of fish, approximately 1 g of subsampled homogenized axial muscle was placed in a Teflon vial. Samples were digested in an alkaline digest prior to derivitization with sodium tetraethylborate to convert nonvolatile MeHg to gaseous methylethylmercury (Bloom 1989). The volatile adduct was then purged from solution and collected onto a graphitic solid (Tenax) trap. The compound was then thermally desorbed from the trap and separated by isothermal gas chromatography separation. After decomposition of the compound to Hg^o, the concentration was determined by cold vapor atomic fluorescence spectroscopy (CVAFS; Bloom and Fitzgerald 1988). For fish, all concentrations are reported on a wet weight basis.

For total Hg analysis of fish, 0.4 g of homogenized tissue was added to a Teflon vial with a 70% sulfuric/30% nitric acid solution and digested overnight at 60°C (Mason and Sveinsdottir 2003). Samples were diluted to 10 mL with distilled deionized water and then further oxidized using bromine monochloride (BrCl). After neutralization of excess oxidant, the Hg concentration was determined by tin chloride reduction, purge and trapping of the Hg^o, and analysis by CVAFS (Sveinsdottir and Mason 2005).

The following QA/QC was performed. Laboratory blanks and duplicates were part of all analytical runs, as were matrix spikes and the analysis of standard reference materials. Blanks were typically a small fraction (<10%; <0.1 ng in the digestate) of the sample concentration (1–1000 ng in the digestate). Detection limits (three times the standard deviation of blank samples) were 0.01 ng g^{-1} for MeHg and 0.05 ng g^{-1} for total Hg.

Analysis of standard reference materials (SRM) typically yielded a value within the certified variance. However, if the SRM was not within the range of the certified value, the sample was reanalyzed. If the value was still not within compliance, the values for that batch of samples were not considered to be reliable, and all samples were reanalyzed. Spike recoveries were done for every batch of samples. This involves the addition of a known amount of standard to a sample prior to the digestion procedure. The comparison of the concentration in the spiked sample and the sample itself allows an estimation of the amount of the analyte in the sample that was recovered.

Saggital otolith pairs were removed from the fish and rinsed in Milli-Q water before being placed into clean polypropylene containers. The otoliths were dried in a laminar flow hood for 48 hours then stored until analysis. Just prior to analysis, the otoliths were cleaned by immersing them in 3% H_2O_2 for 5 minutes and then in 1% HNO_3 for 5 minutes, and were then rinsed copiously with Milli-Q water (Secor *et al.* 2001). The otoliths were weighed before and after cleaning and loss due to cleaning averaged 0.01 g/otolith. The otoliths were then placed into clean polyethylene 15-ml scintillation vials and 1 ml of concentrated HNO_3 was added. After 3 hours, 9 ml of Milli-Q water was added to each scintillation vial. The otoliths were analyzed, after proper dilution, for Sr and Ca by ICP-MS using an internal standard (45 Sc) for Ca only.

Results and Discussion

A Brief Description of the Fish Species Sampled

The dominant food is thought to be fish for largemouth bass and striped bass, although their diets also include invertebrates and other prey (Murdy *et al.* 1997). In a study in the Chesapeake Bay, Walter and Austin (2003) found that overall 44% by weight of the diet of striped bass caught in 1997–1998 was menhaden (*Brevoortia tyrannus*), which is the dominant herring species in estuarine and coastal Mid-Atlantic waters. In the mesohaline waters, mehanden was 60–65% by weight of the striped bass diet in spring, and 55–60% by weight in the fall. Other fish (white perch, croaker, and hake) made up the bulk of the remainder of the diet. Menhaden are filter feeders and because their diet is a mixture of zooplankton and algae, their trophic status is lower than fish that feed more exclusively on zooplankton and other invertebrates, such as croaker and white perch. Diets of striped bass in spring in freshwaters portions of the bay reflected the resident prey. The larger fish (>711 mm) fed mostly on gizzard shad (89% by weight), whereas the smaller fish fed mostly on river herring (50% by weight) and white perch and gizzard shad (20–25% each). Gizzard shad are also filter feeders. For all striped bass, there was a weak correlation between fish size and prey size (Walter and Austin 2003). From historical comparisons, it appears that the fraction of menhaden in the diet of >3-year-old striped bass has decreased over time; from ∼80% in the 1950s to 65% in the 1990s to about 20% currently (Blankenship 2004). Invertebrate prey now forms a larger fraction of their diet than previously (Griffin and Margraf 2003). In addition, it appears that 3–6-year-old fish now weigh 10–15% less for the same size as they did prior to the 1980s. This is shown in Figure 2a, which plots the length–weight relationships for fish sampled in
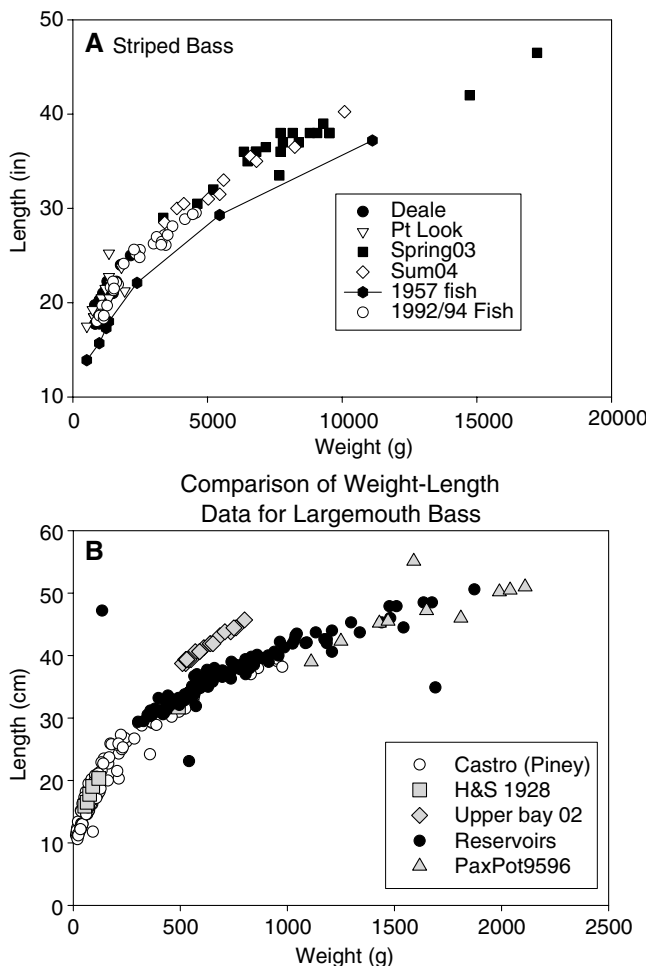
Comparison of Weight-Length
Data for Largemouth Bass

Fig. 2. Relationship between (**A**) striped bass and (**B**) largemouth bass weight and length for different groups of fish caught in various reaches of the mainstem Chesapeake Bay and its tributaries, as well as in the reservoirs. See text for details.

this study, and the fish from 1992 to 1994 (Gilmour and Riedel 2000) compared to fish caught in the 1950s (Mansueti 1961). The 2002–2004 fish appear to have a similar length–weight relationship to the 1992–1994 fish. Clearly, however, fish of similar length now weigh less than they did historically (*i.e.*, the 1950s).

The diet of white perch is mostly invertebrates throughout their lifetime (NOAA 2003; Secor, personal communication). Smaller fish feed on crustaceans and aquatic insects, whereas larger fish prey on crabs, shrimp, and small fish. Although young largemouth bass feed on plankton, insects, and small fishes, the larger individuals are opportunistic and feed on a variety of prey, including crustaceans (crayfish) and fish (Murdy *et al.* 1997). A similar comparison of length–weight data for the estuarine largemouth bass (Figure 2b) shows that the fish were also of relatively low weight compared to fish caught in the bay in 1994 (Gilmour and Riedel 2000) and to reservoir largemouth bass (Sveinsdottir and Mason 2005). The length–weight relationship of the fish caught in 2002 are compared to those reported by Gilmour and Riedel (2000), and some earlier literature values (Hildebrand and Schroeder

1928), and are also plotted against the data for the reservoirs obtained by Mason and Sveinsdottir (2003), and by Mark Castro for Piney Run Reservoir (taken from Sveinsdottir and Mason 2005) (Figure 2b). It is clear that the upper bay 2002 largemouth bass have a lower relative weight than those of all the other datasets.

The largemouth bass analyzed ranged in size from 380 to 450 mm in length, and weighed from 500 to 800 g. White perch sampled ranged in size from 120 to 250 mm and because they were caught in spring, likely represent year 0+ or 1+ fish (Secor, personal communication). The database for white perch was supplemented by the analysis at CBL of fish collected by MDE. White perch are year-round residents of all the tributaries of the Chesapeake Bay, and they usually inhabit waters with a salinity of <18 ppt (NOAA 2003). In the upper bay, the population may be mixed between subestuaries because the salinity is low enough that the fish may migrate between them (Secor, personal communication). They inhabit the shallower reaches in the spring and summer and are found primarily in the deeper channels in winter.

The striped bass caught in the fall of 2002 were overall smaller than those caught in the spring, where large fish were targeted as they enter the bay from the ocean to spawn. Fish as large as 17 kg were caught (range 0.5–17 kg) so that a large size range could be analyzed to determine the extent to which fish Hg concentration increased with age, and whether migration may have a mitigating impact on fish MeHg concentration. Striped bass can be found in the bay all year, and they tolerate a wide range of salinities. They inhabit the deeper waters in the winter and the older fish migrate offshore in the summer, returning to the estuary in the spring to spawn, beginning in early March and continuing until the end of April. Spawning occurs primarily in the upper freshwater reaches of the tributaries to the Chesapeake bay. The striped bass that leave the bay can range widely, and they are distributed along the Atlantic seaboard, from Massachusetts to Cape Hatteras, although they remain in relatively shallow water (Mansueti 1961). Thus, the larger striped bass have a range of life histories.

Fish Mercury and Methylmercury Concentration

Striped Bass. The data for MeHg and total Hg for the striped bass collected from 2002-04 are plotted in Figure 3. There appears, overall, to be a significant increase in fish MeHg and total Hg concentration with fish weight. However, overall, the concentrations are relatively low, especially for the larger fish compared to those of freshwater species of similar trophic status and size. A recent compilation of data of fish Hg concentrations in US waters lists a mean total Hg concentration for Atlantic striped bass of 150 ng g^{-1} ($n = 216$) and a maximum of 840 ng g^{-1}; a mean of 210 and maximum of 400 ng g^{-1} ($n = 19$) for the Gulf Coast; and a mean of 460 and maximum of 900 ng g^{-1} ($n = 26$) for the Pacific Coast (Cunningham *et al.* 2003). Data for striped bass in San Francisco bay fall within these values as well (Greenfield *et al.* 2003). Striped bass in the Hudson River averaged 360 ng g^{-1} and ranged from <50 to 1200 ng g^{-1} (HRF 2004). Thus, the current dataset is consistent with the average Atlantic value,
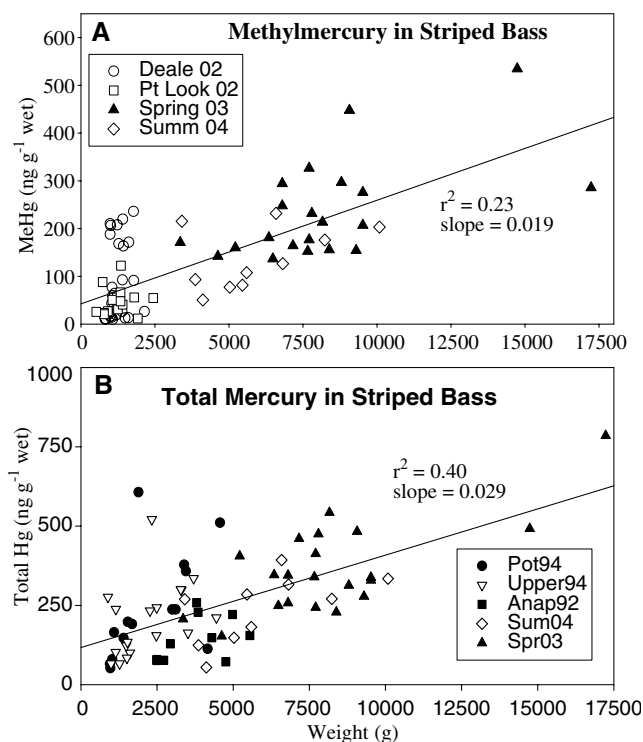
Fig. 3. Plot of the concentration of (**A**) methylmercury (MeHg) and (**B**) total mercury (Hg), both in ng g^{-1} (ppb) wet weight, in striped bass from the Chesapeake Bay against fish weight. Data from this study and from Gilmour and Riedel (2000).

for which no information is provided on fish length or weight. The data collected for total Hg in 2003–2004 can be compared to concentrations of total Hg in striped bass from earlier studies in 1992 and 1994 by Gilmour (1999) (Figure 3b). The data for 1992 are from fish caught in the vicinity of Annapolis (Anap92). The 1994 data are from either the Potomac River (Pot94) or in the vicinity of Annapolis (Upper94). Overall, there appears to be some difference, even given the scatter in the data, between the fish sampled 10 years apart, with the earlier collected fish having somewhat higher concentrations.

The slopes of the relationships for the various sample collections of fish for total Hg and weight are all very similar (Table 1). The greatest slopes are for the 1994 upper bay and Potomac River fish. The relationship for all of the 1994 fish was also significant (r^2 = 0.23; slope = 0.058 (ng g^{-1}) g^{-1}) and substantially higher than that for the 2002–2004 fish (r^2 = 0.55; slope = 0.036 (ng g^{-1}) g^{-1}). The differences in the correlation slope suggest that striped bass were accumulating more Hg 10 years ago than at present. There are little actual data for Hg inputs to the Chesapeake bay over this time period that may be used to corroborate or refute an inference that differences in fish tissue levels is due primarily to changes in Hg inputs. However, such a change would be consistent with regulation of atmospheric Hg sources in Maryland and elsewhere in the United States, and in likely decreased inputs of Hg from point sources to the bay.

Correlations between fish weight and concentration were also sought for the individual datasets and for the entire dataset for MeHg (Table 1). No MeHg measurements were made by

Gilmour and Riedel (2000). For the smaller datasets, the relationships were not significant. For MeHg, the overall relationship had a relatively flat slope (0.022 (ng g^{-1}) g^{-1}), which was similar to that of the spring 2003 fish. For total Hg, the overall slope of the regression line was higher than that for MeHg, suggesting that total Hg concentration is increasing relatively more rapidly than MeHg in these fish. This is shown more clearly in Figure 4, where the fraction of the total Hg as MeHg decreases with increasing total Hg concentration. It would be expected that if larger striped bass fed almost exclusively on planktivorous fish, they should have the majority of the Hg in their muscle tissue as MeHg. However, this is only so for fish of <200 ng g^{-1} wet weight total Hg. That the fraction as MeHg decreases with increasing total Hg, and, by correlation, with size, is unusual because it would rather be expected that the fraction as MeHg would increase, if anything, with increasing size because this has been shown for many species of fish.

There are a number of potential reasons for this trend. Food preference may be an important factor if striped bass feed more predominantly on menhaden as larger fish than on other planktivorous species, or have a different diet when in coastal waters. Although the data on feeding habits is somewhat limited, it appears that menhaden tend to have a higher fraction of algae in their diet than other planktivorous fish (NOAA 2003). Our limited sampling and analysis of anchovies in the Chesapeake bay in 1997 showed that their MeHg concentration was low, <10 ng g^{-1} (Table 2), within a similar range to invertebrates such as the blue crab, and somewhat higher than zooplankton and amphipods (<5 ng g^{-1}). If anchovies were feeding exclusively on zooplankton, then their concentration would be expected to about five times higher, reflecting the higher trophic level (Watras and Bloom 1992; Mason *et al.* 1996). Their relatively low concentration is consistent with a diet that is not exclusively zooplankton. It would be expected that the MeHg concentration in menhaden would be similar to or lower than that of anchovies.

It is generally assumed that essentially all the Hg in fish muscle tissue of upper food level consumers is MeHg, and this assumption is primarily based on an early study by Bloom (1992). However, there is evidence in the literature that this is not always the case, and a number of recent publications have shown this not to be true, especially for estuarine and coastal fish (Baeyens *et al.* 2003; Riget *et al.* 2000; Kannan *et al.* 1998; this work). Kannan *et al.* (1998) examined the concentration of Hg and MeHg in numerous fish species in South Florida estuaries and found low fractions of MeHg in catfish (56–100% MeHg) and spot (54–100%). Most other fish species had >80% MeHg. Baeyens *et al.* (2003) showed that species resident in the Scheldt estuary had lower %MeHg (flounder 67% and plaice 64%) than coastal (flounder 82%, plaice 84%, dab 83%, and whiting 87%) and North Sea fish (plaice 97%, dab 97%, and whiting 91%). Thus, the %MeHg in plaice decreased from about 97% for North Sea fish to 84% for Belgium coastal fish to 64% for fish from the Scheldt estuary. In addition, the MeHg concentration was lowest in the Schedlt estuary fish, even though this is considered to be a relatively polluted river (Baeyens and Leermarkers 1996, Baeyens *et al.* 2003). It is likely that the differences in %MeHg reflect differences in feeding strategies. The results found for striped bass for %MeHg in this study (68 ± 24% for 2003 fish; 61 ± 19% for 2004 fish) are comparable.

Table 1. Regression data for striped bass for either total mercury (Hg) concentration and weight, or methylmercury (MeHg) concentration and weight

Sampling location and time	n	Slope (ng g^{-1})	Intercept(ng g^{-1})	Regression coeff., r^2	Signif.
Total mercury					
Spring 03 mid/upper	21	0.033	94.1	0.50	<0.01
Summer 04 mid/upper	10	0.031	52.8	0.37	<0.05
Potomac Fall 94	14	0.069	80.1	0.27	0.05
Upper bay fall 94	18	0.047	99.3	0.19	<0.1
Annapolis fall 92	10	—	—	0.19	NS
All fish	73	0.031	117	0.40	<0.01
Methylmercury					
Spring 03 mid/upper	21	0.019	74.5	0.34	<0.01
Summer 04 mid/upper	10	—	—	0.20	NS
Deale 02	32	—	—	0.051	NS
Sp Lookout 02	15	—	—	0.012	NS
All fish	77	0.022	42.4	0.54	<0.01

NS = not significant.
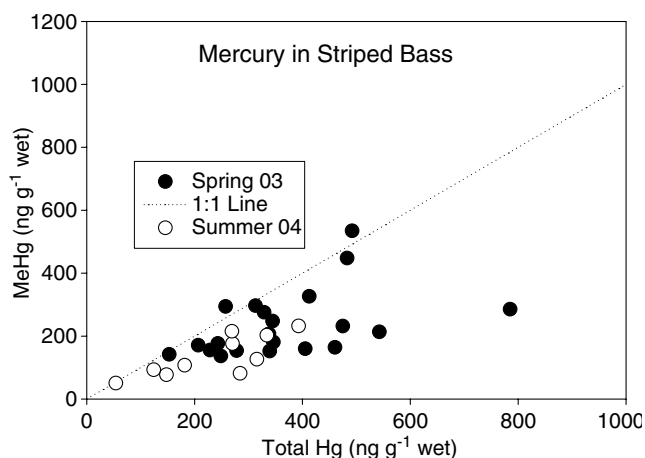
Fig. 4. Relationship between total mercury (Hg) and methylmercury (MeHg) for striped bass caught in the Chesapeake Bay in 2003 and 2004

Furthermore, a detailed study by Holsbeek et al. (1997) showed that a variety of relationships exist between fish size and Hg and MeHg content. For the majority of species, there was an increasing level of MeHg in tissue with increasing age, with an overall low and relatively constant inorganic Hg burden. So, for these fish essentially all the muscle tissue is MeHg, regardless of age. Alternatively, for some species, the fraction as MeHg increased with age. However, there also appeared to be a relative increase in inorganic Hg relative to MeHg with age for some species of fish, such that the %MeHg decreased with age. In the study of Holsbeek et al. (1997), this pattern was found with two planktivorous fish (*Hilsa* and *Ilisha*). Kannan et al. (1998) found a weak correlation ($r = 0.24$; $p < 0.1$) between %MeHg and total Hg for the fish species they examined from the Florida estuaries. Low %MeHg in fish has also been reported for large open ocean fish such as blue marlin, and other species from the Northern Barents Sea (as reported by Holsbeek et al. (1997)). For these earlier studies, the potential for locally high inorganic Hg inputs were ruled out as an explanation for the relatively high inorganic Hg content, and this would also be true for the Chesapeake Bay.

In another study, Riget et al. (2000) found that the fraction of total Hg as MeHg in Arctic char varied strongly between land-locked lake resident populations (91.5 ± 2.1%) and anadromous fish that entered rivers in close proximity to the lakes (72.3 ± 2.0%). Also, the migratory fish had a much lower MeHg concentration (median size adjusted values for anadromous fish of 23–80 ng g^{-1}) than the resident fish (130–670 ng g^{-1}). This trend is similar to what was found in this study in that the Chesapeake bay striped bass have lower concentrations than those found in Liberty Reservoir (limited sampling ($n = 5$) range 670–2932 ng g^{-1} total Hg for fish of 3600–16400 g; Gilmour 1999). Also, as discussed below, the estuarine largemouth bass had a lower MeHg burden than reservoir fish of the same size (Table 2). In all cases, the overall difference in tissue concentrations was at least a factor of five.

With the Arctic char, there was a distinct difference in the rate of growth of the fish with resident lake populations, ranging in size from 24 to 48 cm, being 11–19 years old compared to the estimated age of anadromous fish of 36 to 40 cm, of 6–7 years (Riget et al. 2000). Clearly, the slower-growing land-locked fish were accumulating relatively more MeHg than the faster-growing migratory fish. Thus, growth dilution may be an important factor, although it is also possible that differences in food source may account for the differences in fish MeHg concentration.

There is also the possibility of a demethylation process being present in these fish. Although such an idea is intriguing, the species for which a decreasing %MeHg with size has been found cover a wide range of species and different locations, and the notion of demethylation is therefore somewhat difficult to reconcile. Further research is clearly needed to examine the potential for MeHg demethylation by fish. Such a process has been postulated to occur in the liver of mammals and birds (for example, Wagemann et al. 1998; Kim et al. 1996). For the striped bass, the most likely alternative explanation, besides demethylation, for the data is that there are changes in diet with age that lead to these fish essentially feeding lower on the food chain, and on fish of lower concentration because they are feeding mostly off-shore. This is driven mainly by the preference of large fish for menhaden (Walter and Austin 2003), which, being filter feeders, feed on both zooplankton and

Table 2. Concentration of methylmercury on a wet weight basis for fish recently caught in Maryland waters

Common name	Size (cm)	MeHg(ng g^{-1} wet)	%MeHg	No. of fish	Ref.
Fish in reservoirs					
Largemouth bass	30–56	310 ± 290	95 ± 35	225	1
Smallmouth bass	30–43	360 ± 160	91 ± 25	18	1
Bluegill	13–25	70 ± 80	80 ± 36	97	1
Crappie	15–30	90 ± 60	83 ± 45	49	1
Estuarine Fish[a]					
Channel catfish	36–75	13–21	—	20[b]	3
White perch	18–25	2–104	28 ± 14	21[c]	2,3
Striped bass	38–107	120 ± 100	65 ± 22	79	2
Carp	∼50	26	—	1[b]	3
Largemouth bass	38–43	14 ± 7	—	16	2
Yellow perch	∼25	13	—	1[b]	3
Eel	∼50	10	—	1[b]	3
Anchovy		4–8		3[b]	4
Invertebrates[a]					
Blue crab		2–11	55 ± 19	5	3
Clams	Various	<1–2	<5	many	5
Copepods	>202 μm	1–4	—	5[b]	4
Amphipods		<1–3		Mixed	5

Notes: All samples were analyzed at CBL under this project, during previous MD DNR funded studies (Mason and Sveinsdottir 2003), and from samples collected by MDE (unpublished data) and by this research group (unpublished data), and other sources (Mason and Lawrence 1999). References: 1 = Mason and Sveinsdottir (2003); 2 = Data from this study; 3 = fish analyzed for MDE by CBL, unpublished data; 4 = samples collected and analyzed by this research group in 1997, unpublished data; 5 = clams collected in the vicinity of Hart-Miller Island and data from Mason and Lawrence (1999). Note that earlier data from Gilmour (1999) is not included here because no methylmercury measurements were made in that study.
[a] Data for both saline and tidal fresh portions of the Chesapeake Bay.
[b] The number represents the number of composite samples of 1–5 fish, or invertebrates.
[c] The data are a combination of 21 composite samples of 1–5 fish, and 30 individual fish.

algae. Thus, they are at a somewhat lower trophic level than the fish consumed by younger striped bass, such as white perch, which mainly consume invertebrates. Finally, given the relatively low fraction as MeHg in the striped bass, it is clear that measurements of only total Hg in striped bass, and other similar coastal fish, may be inadequate if risk based on MeHg is to be evaluated because this could lead to an overestimation of contamination levels.

Largemouth Bass. The range in fish weight for the largemouth bass was relatively small, and thus it is harder to make definitive statements about the relationship between weight and concentration. The MeHg concentrations found were low (14 ± 7 ng g^{-1}; $n = 16$). Indeed, in comparison to the fish concentration data for largemouth bass from Maryland reservoirs (Sveinsdottir and Mason 2005), there is an obvious and substantial difference in concentration for fish of similar weight (Tables 2 and 3). However, there was also a substantial variability between reservoirs in this relationship (Sveinsdottir and Mason 2005; Table 3). Gilmour (1999) reported total Hg concentrations for largemouth bass caught in the Potomac and Patuxent Rivers in 1995 and 1996. These data are for heavier fish and show a higher slope for the relationship between fish weight and total Hg concentration (Table 3). A comparison of the earlier and more recent datasets could be made if it is assumed that all the Hg in the estuarine largemouth bass is MeHg. This is indeed the case for the reservoir fish (Mason and Sveinsdottir 2003; Table 2) but, based on the discussion above, this may not be so for the estuarine fish.

The slope of the correlation line for the previous total Hg versus weight data for largemouth bass is about a factor of two higher than that of the upper bay fish for MeHg, and about a factor of four lower than the reservoir fish (Table 3). A comparison between the concentration of MeHg in the reservoir largemouth bass with those of the estuarine fish shows that, on average, the concentration in reservoir fish is about three to five times greater than that of the estuarine fish (Table 2; Sveinsdottir and Mason 2005). Furthermore, the average slope of the relationship for the reservoir fish (slope = 0.38 (ng g^{-1}) g^{-1}) is greater and thus the disparity increases with fish weight. However, the slopes for the relationship between weight and MeHg concentration varied greatly between reservoirs from being very low (<0.1 (ng g^{-1}) g^{-1}) to nearly 0.9 (ng g^{-1}) g^{-1} (Table 3). Thus, the estuarine data are at the lower end of the variability for freshwater bodies.

Differences in growth rates and feeding patterns between the two types of ecosystems (reservoir and estuarine) or differences in exposure concentration could account for the differences in fish MeHg. The concentration of MeHg in the waters of the reservoirs is generally higher than that of the estuary (Sveinsdottir and Mason 2005; Sveinsdottir 2002; Mason *et al.* 1999), and thus the differences could be ascribed to differences in the exposure regime. Concentrations of MeHg in the Chesapeake bay waters are typically <0.1 ng/L, whereas concentrations in the reservoirs ranged up to 0.4 ng/L, with some higher concentrations on occasion. There can therefore be up to an order of magnitude difference in MeHg concentrations between systems, and this could mostly account for the differences observed. For the reservoirs, largemouth bass

Table 3. Regression data for largemouth bass collected in the Chesapeake Bay and in the reservoirs of Maryland

Sampling location and time	Regression slope (ng g^{-1}) g^{-1}	Regr. Coeff., r^2	Significance
Methylmercury			
Maryland Reservoirs 2000–2001	0.38	0.29	<0.01
Savage Reservoir (high MeHg in fish)	0.86	0.27	<0.05
Conowingo Dam (low fish MeHg)	0.09	0.41	<0.01
Upper Chesapeake 2002	0.04	0.31	<0.01
Patuxent/Potomac Rivers 1994/1995[a]	0.10	0.31	<0.05

Note: Data for the reservoirs taken from Sveinsdottir and Mason (2005).

[a] Assuming that all mercury is methylmercury.

MeHg concentration correlated best with surface-water-filtered MeHg concentration (Sveinsdottir and Mason 2005).

White Perch. For the white perch, the populations sampled had somewhat different concentrations, with the fish from the Choptank River having higher and more variable MeHg concentrations than fish from the Severn River (Figure 5). The fish from the Patapsco had intermediate concentrations, although they were more similar to those of the Choptank fish. Only the dataset for the Severn resulted in a statistically significant relationship ($r^2 = 0.45$; slope = 0.090 (ng g^{-1}) g^{-1}). Of all the white perch analyzed, the highest relative MeHg concentrations were found in fish from the eastern shore rivers (Figure 5). The Potomac River also had some fish with relatively higher concentrations. In comparison, white perch from the Hudson River estuary had somewhat higher total Hg concentrations (mean 230 ng g^{-1}; range 10–610 ng g^{-1}; size information not available; HRF 2004). The mean total Hg value reported by Cunningham *et al.* (2003) for the Atlantic coast is 180 ng g^{-1}; max 1200 ng g^{-1}, $n = 157$).

The white perch MeHg concentrations are relatively low for all the datasets (<120 ng g^{-1} wet weight), and this is possibly due to the relatively small size of the fish relative to the striped bass. However, the white perch do not attain a size similar to that of the other species. For all the fish species examined here, MeHg concentrations are generally in the <100 ng/g wet weight range for fish <500 g in weight. However, comparison of the slope of the concentration–weight relationship for the white perch and the striped bass shows that the rate of increase in concentration per gram of tissue is higher for the white perch than for the striped bass.

Again, white perch was also analyzed by Gilmour (1999) for total Hg; fish were mostly from the Patuxent, with one fish from the Severn River. These data can be compared with the total Hg data for the Patapsco River fish (Figure 5b), because these were the only samples analyzed for both total Hg and MeHg in this study. Although the fish from the Severn was larger than the current fish at 340 g, its concentration was low (63 ng g^{-1}), and this fits with the Potomac River dataset and the 1994 Patuxent River data, except for the one outlier: a fish with more than 400 ng g^{-1} total Hg. As mentioned earlier, the mid and upper bay salinities may be low enough seasonally that there is the potential for migration of white perch between subestuaries, and therefore all the upper bay fish may represent the same population.

The Patuxent and Potomac River fish are likely different populations, but there is no clear difference overall between
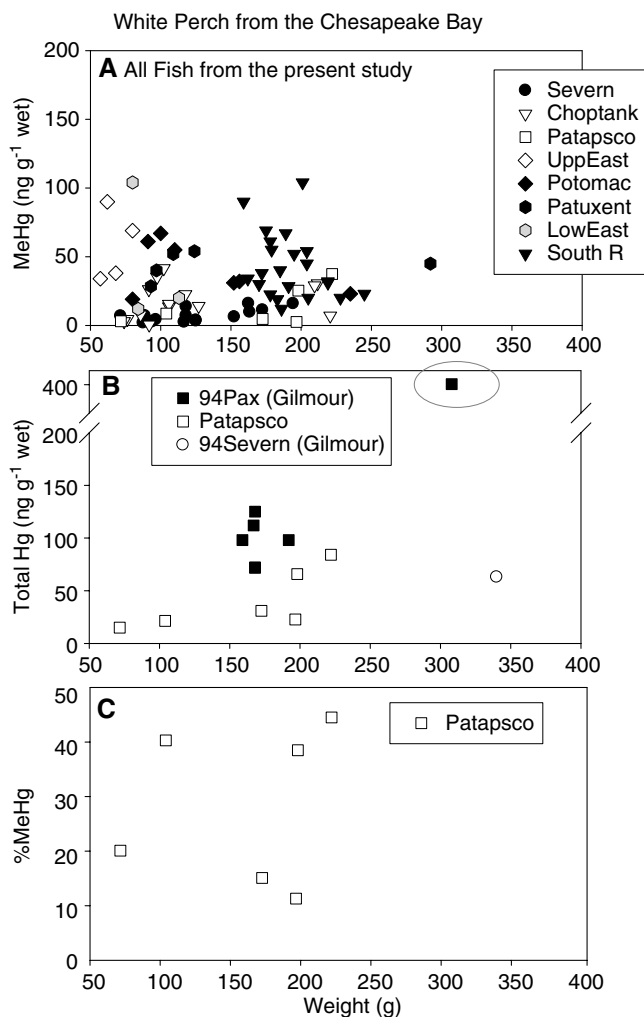

Fig. 5. Plot of the concentration of (**A**) methylmercury (MeHg), (**B**) total mercury (Hg), both in ng g^{-1} (ppb) wet weight, and (**C**) percent MeHg in white perch from the Chesapeake Bay against fish weight. Data from this study and from Gilmour and Riedel (2000)

the various populations in total Hg concentration. The data for white perch, although limited, indicate a relatively low %MeHg in these fish (Figure 5c). This likely reflects the fact that these smaller fish are not piscivorous but have a large proportion of their diet being invertebrates. There are very little data in the literature on the fraction of total Hg as MeHg in white perch and striped bass, species that belong to the same

genus. However, from the data presented here, it appears that both species have a relatively low fraction of the total Hg as MeHg, a fraction that appears to belie the assumed trophic status for striped bass. As discussed above, the low fraction as MeHg in the tissue can be explained in terms of diet if both species are feeding to a large degree on invertebrate prey and/or on filter-feeding fish.

Methylmercury Bioaccumulation. For the fish species examined here, it is somewhat difficult to compare among species in terms of MeHg concentrations because the fish vary substantially in size. In terms of health risk, the size of the fish consumed is not relevant for the different species, and thus concentration is the most useful metric. Indeed, the results of this study confirm that it is both the trophic status of the fish and its age that are important determinants in terms of its MeHg concentration. This notion was clearly shown in an earlier study where predatory insects in Maryland mountain streams had a higher MeHg burden and a higher %MeHg than fish and crayfish from the same stream that had omnivorous habits (Mason *et al.* 2000). Indeed, given this variability, it is likely better to consider the slope of the regression line for the relationship between age, or the age proxy (weight or length), and the MeHg concentration to understand the accumulation of MeHg in fish across habitats and species. This provides a measure of the rate at which MeHg is being accumulated as the fish ages. Of course, the relationships between fish length, weight, and age are not truly linear, so there is some limitation to the usefulness of this approach. However, it is clear from the data presented here that none of the estuarine fish species examined are accumulating MeHg (for all species, slope <0.1 (ng g^{-1}) g^{-1}) at rates comparable to that of the reservoir largemouth bass (0.38 (ng g^{-1}) g^{-1} on average (Sveinsdottir and Mason 2005). It is hypothesized that such differences can be to a large degree explained by differences in MeHg water concentrations, which are overall higher for the reservoirs (0.01–0.4 ng L^{-1}, typically) than in the bay (0.01–0.1 ng L^{-1}; Mason *et al.* 1999). As discussed by Sveinsdottir and Mason (2005), the reservoir largemouth bass MeHg concentration was most strongly related to MeHg levels in the water, although other variables were also important. Thus, water concentration alone may account to a large degree for the lower concentrations of MeHg in the estuarine largemouth bass compared to the reservoir fish, and similarly for land-locked striped bass (Gilmour 1999), and for the relatively low concentration and rate of accumulation in the striped bass and white perch in the estuary (Figures 2–5; Table 2). This conclusion is predicated on the assumption that the food consumed by the fish in the different environments is of a similar trophic level. Clearly, if fish in reservoirs are feeding at a different trophic level than fish in the estuary, then this could also be a major factor in the differences in fish concentration.

The concentrations of MeHg in fish and invertebrates from the Chesapeake bay are given in Table 2. Concentrations are low for small invertebrates, such as copepods and amphipods (<5 ng g^{-1} wet weight) (Mason and Lawrence 1999), and thus organisms feeding on them, such as anchovies and menhaden, should have low MeHg burdens as a result. The bioaccumulation factor per trophic level for MeHg is about three to five

(Mason *et al.* 1996; Watras and Bloom 1992), so that fish feeding exclusively on invertebrates should have MeHg burdens of <25 ng g^{-1} wet weight. This is indeed the case with anchovies, which feed to a large degree on copepods (NOAA 2003), which have concentrations in the range of 4–8 ng g^{-1} wet weight compared to their prey of 1–4 ng g^{-1}. Large invertebrates, such as crabs, have burdens a factor of two to three higher (2–11 ng g^{-1}), reflecting their more omnivorous, scavenging nature. In contrast to blue crabs, crayfish from the MD reservoirs had higher MeHg burdens, averaging 22 ± 14 ng g^{-1} wet weight (range 7–45 ng g^{-1} wet weight) (Sveinsdottir and Mason 2005). Such differences lower in the food chain between the reservoirs and the estuary are consistent with the higher concentrations found, for example, for largemouth bass in the reservoirs.

For the estuarine species examined here, white perch of the size analyzed are the fish likely to be feeding on invertebrates, with their diet supplemented by small fish. Most of the fish had MeHg concentrations of <40 (ng g^{-1}) g^{-1}, which indicates a diet mostly consisting of crabs and other invertebrates. In contrast, largemouth bass are likely feeding on a mixture of invertebrates and fish. Their MeHg burden reflects this. The diet of the largemouth bass in reservoirs had a higher MeHg burden (Sveinsdottir and Mason 2005). Small fish in the reservoirs had MeHg levels of 9–45 ng g^{-1} for fish <10 cm (4 inches), similar to that of crayfish, so that fish feeding on these fish would be expected to have a burden of up to 250 ng g^{-1}. Clearly, the larger largemouth bass in the reservoirs must be feeding on larger fish. The average MeHg concentration for the largemouth bass in this study, which ranged in size from 38 to 45 cm (15–18 inches) was 14 ± 7 ng g^{-1} wet weight. Although no stomach content analysis was done, such levels reflect a diet that must be dominated by invertebrates. If fish were the dominant food, higher concentrations would be expected based on the measured concentrations of MeHg in the various estuarine species (Table 2).

The larger striped bass are thought to feed almost exclusively on fish such as menhaden and anchovies, as discussed above, and therefore, based on simple food web bioaccumulation estimations, should have MeHg levels of 100 ng g^{-1} or greater. Such an estimation is consistent with the measured burdens in the fish. Clearly, as fish retain MeHg as they grow, their burden increases with age and the simple bioaccumulation factor approach is not sufficient to explain all the variability in concentration. A detailed bioenergetics model would be needed to further examine the interrelationships between prey and predator MeHg concentrations.

In summary, the concentrations of MeHg in small fish and invertebrates caught in the Chesapeake bay are lower than those of comparable organisms from MD reservoirs. The differences are consistent with the magnitude and direction of the differences in MeHg concentrations in the water. It appears that the lower MeHg concentration in estuarine water is the primary reason why fish from the estuarine waters have relatively lower MeHg burdens. The differences in MeHg levels in the water are not directly related to levels of Hg in atmospheric deposition, because these inputs are relatively similar across the state for locations away from local inputs (Mason *et al.* 2000). Thus, the reservoirs appear to be able to produce and transport more MeHg from sediments to the food chain; the concentration differences depend on surface area/volume

considerations; the residence time of water in the reservoirs is longer, and/or the relative extent of wetlands and other locations where methylation is enhanced.

Otolith Chemistry and Methylmercury in Striped Bass

The incorporation of elements into fish otoliths, which are essentially calcium carbonate ($CaCO_3$), occurs with the incorporation rate being related to water chemistry in some instances, whereas in other cases there is no relationship (Secor *et al.* 2001). Strontium (Sr) is one element that is incorporated into the otolith lattice, and Sr:Ca ratios have been used as a salinity proxy. Ocean Sr:Ca molar ratios in seawater are between 8.5 and 9 mmol mol^{-1}, and freshwater values tend to be much less (typically <5), although they can be highly variable (Kraus and Secor 2004). In a detailed study of striped bass in the Hudson River, Secor *et al.* (2001) determined that the Sr:Ca ratio of otoliths was a reliable indicator of the striped bass life history. Fish that spent the majority of their lives in the open ocean, only returning to the estuary yearly to spawn, had the highest ratio, on the order of 6 to 6.5 mmol mol^{-1}. This molar ratio is similar to that of seawater. On the other hand, Secor *et al.* (2001) found that resident striped bass in the Hudson River had Sr:Ca in otoliths of <2, with an average of 1.4 mmol mol^{-1}, which was determined to be equivalent to an average salinity of 2 ppt. Fish that inhabited the mesohaline Hudson River and did not migrate offshore had Sr:Ca in otoliths of 4–5.4 mmol mol^{-1}, which is deemed equivalent to salinities of 13 to 20 ppt. It would be expected that striped bass in the Chesapeake bay would show similar variability.

There is variability in the Sr:Ca values for different rivers, however, and this could limit the usefulness of the proxy if the river concentration is elevated and near that of seawater (Kraus and Secor 2004). Indeed, these authors noted that the Choptank River is one local environment with a Sr:Ca ratio relatively similar to that of seawater (at Greensboro, average ratio is 4.9 mmol mol^{-1}; USGS 2004). For the Susquehanna River, measurements at the Conowingo Dam show a range of values from 2.5 to 3.5, with an average of 2.8 mmol mol^{-1}. Indeed, otoliths of largemouth bass from the upper bay were analyzed under this project and the values fall within this range, from 1.4 to 4.0, with an average of 2.5 ± 0.5 mmol mol^{-1}. For other major tributaries, the ratio for water varies between 2 and 3 mmol mol^{-1} (Patuxent at Bowie 2.2; Potomac at Chain Bridge 2.4; Rappahannock at Fredericksburg 3.1 mmol mol^{-1}).

Thus, striped bass that predominantly inhabit the mid-to-upper bay region, and do not migrate offshore, should have otolith Sr:Ca values of 3 mmol mol^{-1} or less, except if they inhabited the upper reaches of the Choptank River for extended periods, whereas the fish that spent extended periods offshore would have ratios of 6 mmol mol^{-1} or greater. The Sr:Ca ratio was measured in a number of otoliths taken from striped bass sampled in 2002 at Deale and Point Lookout, and in spring 2003. The data are plotted in Figure 6 against the fish weight and the fish MeHg concentration. The plots show the relationship between these three variables for the striped bass caught at different times and different locations. For the fish caught in 2002, there appears to be two populations in terms of Sr:Ca ratio: one with values of 2–4 mmol mol^{-1}; the other with
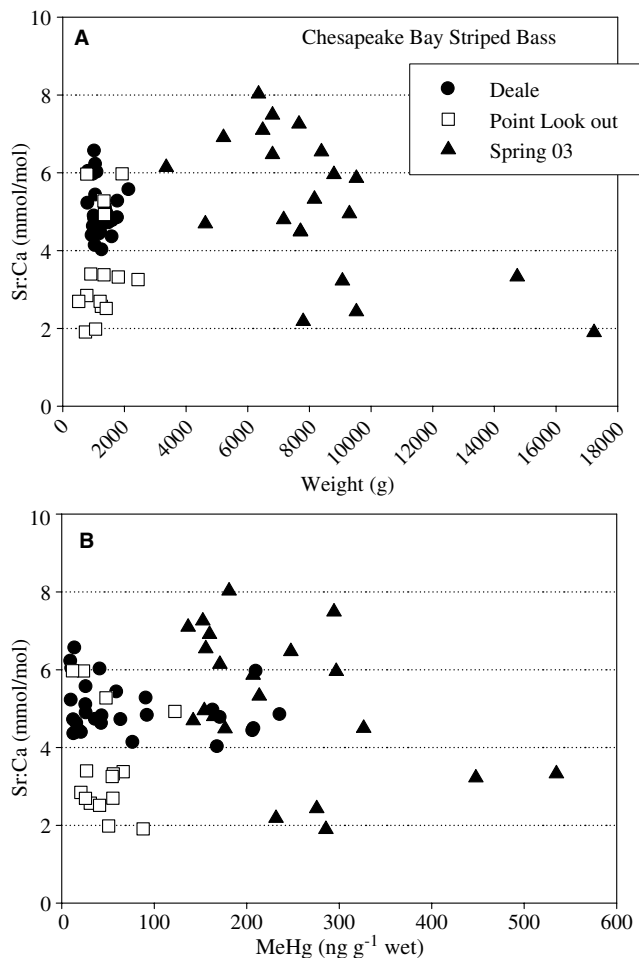

Fig. 6. (**A**) The relationship between fish weight and strontium:calcium ratio (Sr:Ca) and (**B**) methylmercury and Sr:Ca for striped bass caught within the mainstem Chesapeake Bay. Diamonds represent fish caught at Deale; squares are fish from Point Lookout; and triangles are fish caught in spring 2003.

values from 4 to 6 mmol mol^{-1}. The higher ratios are mostly associated with the fish caught at Deale and likely represent fish that are resident of the Upper bay and its tributaries. As noted above, and based on the USGS data available, it appears that the rivers of the eastern shore, and especially the upper eastern shore (Choptank and Chester Rivers, for example) have Sr:Ca ratios for their freshwater reaches that can exceed 4 mmol mol^{-1}. In contrast, the Susquehanna River has a relatively low Sr:Ca ratio of 2.8 mmol mol^{-1}. Thus, the higher ratios for these fish do not necessarily suggest that they are migratory fish. Indeed, these fish are likely to be residents of the bay.

Fish caught in spring 2003, where otoliths were analyzed, were all >3 kg. However, their Sr:Ca values ranged from around 2 to nearly 8 (Figure 6). Four of the largest fish had low values (< 4 mmol mol^{-1}), and this suggests that these were fish that resided dominantly in the mainstem upper bay. The fish of intermediate size, 4–9 kg, had the highest Sr:Ca ratios and these likely represent migratory fish because, even though the rivers of the Chesapeake bay have relatively high Sr:Ca ratios, none are >5 mmol mol^{-1}. Finally, there is a group of large fish with intermediate Sr:Ca ratios that cannot be dis-

tinguished as being either resident or migratory based on the analysis performed.

The largest fish had the highest MeHg concentrations (Figure 6). The reason for this could be related to purely size-related effects, because there was a significant relationship between fish weight and MeHg content for striped bass (Figure 3). The alternative explanation is that these are fish that spend relatively more of their time in the bay than offshore, as suggested by their Sr:Ca ratio, and that they are therefore exposed to higher MeHg levels and thus contain a higher MeHg burden. Although estuarine MeHg concentrations are low, those of the open ocean are even lower and mostly undetectable (<0.01 ng/L) (Mason and Fitzgerald 1996).

As suggested above, it would be expected that fish that spend the majority of their life offshore should have a lower MeHg burden that those that remain in the estuary, given the higher MeHg concentrations in sediment and water in the Chesapeake bay compared to the shelf and open ocean waters (Mason *et al.* 1999; Mason and Fitzgerald 1996). However, examination of Figure 6 suggests that there is no strong evidence for this, and there is little relationship between Sr:Ca and fish MeHg. These results suggest that there must be a number of conflicting factors that confound the usual relationship. Clearly, the relatively high Sr:Ca ratios, and the high variability in the ratio for the tributaries of the Chesapeake Bay, limit the usefulness of this technique in assessing migratory patterns in this instance.

In summary, although otolith analysis provides some indication of patterns of migration in Chesapeake bay striped bass, and confirms the conclusions of Secor *et al.* (2001) that striped bass have fairly divergent life history traits, it does not provide a clear picture of higher exposure for estuarine fish. Clearly, migration is a confounding factor in determining the age–MeHg relationship because not all striped bass have the same life history in terms of their mobility over time. Also, separation of striped bass by sex could allow better determination of life history because larger (>4 kg) female fish are more likely to migrate.

Conclusions

Concentrations of MeHg in striped bass caught in the Chesapeake bay and its tributaries show a relationship with fish weight. However, fish of more than 5 kg still have relatively low MeHg burdens compared to fish that inhabit Maryland reservoirs. Considering 300 ng g^{-1} as a reasonable regulatory value for average fish consumption, it is clear that most fish analyzed are below this limit. Thus, regulation of striped bass may not be required at the same level for these fish as has been promulgated for Maryland reservoir fish. The concentrations of MeHg in largemouth bass caught in the tidal tributaries of the Chesapeake bay are lower than largemouth bass residing in reservoirs, for fish of similar size. Thus, this confirms the notion that estuarine fish accumulate less MeHg than fish in reservoirs or lakes, likely primarily as a result of lower MeHg levels in estuarine waters. Although levels of MeHg are lower in largemouth bass from the tidal tributaries, the concentrations do increase with age such that the larger fish (>2 kg) will have levels greater than 300 ng g^{-1}. For white perch, levels of MeHg were low, especially for fish from the upper reaches of

the bay. For most fish analyzed, MeHg concentrations were <100 ng g^{-1}.

Otolith analysis showed that striped bass caught in the mainstem Chesapeake bay came from both resident and migratory populations. There was, however, insufficient statistical difference in MeHg concentration between these sub-populations. This confounded interpretation and limited the conclusions about the role of migration in influencing MeHg levels in striped bass from the Chesapeake Bay. Overall, the estuarine fish (striped bass and white perch) appeared to have a lower %MeHg in their tissues than would have been predicted based on previous results. Other recent studies have found similar trends. The reason for this requires further investigation.

References

Baeyens W, Leermarkers M (1996) Particulate, dissolved and methylmercury budgets for the Scheldt estuary (Belgium and the Netherlands). In: Baeyens W, et al. (eds) Global and regional mercury cycles: sources, fluxes, and mass balances. Kluwer Academic Publishers, Dordrecht, The Netherlands. pp 285

Baeyens W, Leermakers M, Papina T, Saprykin A, Brion N, Noyen J, De Gieter M, Elskens M, Goeyens L (2003) Bioconcentration and biomagnification of mercury and methylmercury in North Sea and Scheldt estuary fish. Arch Environ Contam Toxicol 45:498–508

Benoit JM, Gilmour CC, Heyes A, Mason RP, Miller CL (2003) Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In: Biogeochemistry of environmentally important trace elements. American Chemical Society Publ, ACS symposium series 835, pp 262–297

Benoit JM, Gilmour CC, Mason RP, Heyes A (1999) Sulfide controls on mercury speciation and bioavailability in sediment pore waters. Environ Sci Technol 33:951–957

Benoit JM, Gilmour CC, Mason RP, Riedel GS, Riedel GF (1998) Behavior of mercury in the Patuxent estuary. Biogeochem 40:249–265

Benoit JM, Mason RP, Gilmour CC (2001) Aspects of the bioavailability of mercury for methylation in pure cultures of *Desulfobulbous proprionicus* (1PR3). Appl Environ Microbiol 67:51–58

Blankenship K (2004) Menhaden stock perplexes fish managers. bay J 14(6). www.bayjournal.com/04-09/menhaden.htm

Bloom NS (1989) Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. Can J Fish Aqua Sci 46:1131–1140

Bloom NS (1992) On the chemical form of mercury in edible fish and marine invertebrate tissue. Can J Fish Aqua Sci 49:1010–1017

Bloom NS, Fitzgerald WF (1988) Determination of volatile species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. Analytical Chim Acta 208:151–161

Cunningham P, Cooter W, Sullivan E (2003) Mercury in marine life database. Prepared by RTI International for USEPA, April 2003

Driscoll CT, Blette V, Yan C, Schofield CL, Munson R, Holsapple J (1995) The role of dissolved organic carbon in the chemistry and bio availability of mercury in remote Adirondack lakes. Water Air Soil Poll 80:499–508

Fitzgerald WF, Clarkson T (1991) Mercury and monomethylmercury—present and future concerns. Environ Health Perspect 96:159–166

Gilmour CC (1999) A preliminary survey of size-specific mercury concentrations in game fish from Maryland fresh and estuarine waters. Chesapeake bay and watershed programs: monitoring and non-tidal assessment CBWP-MANTA-AD-98-9

Gilmour CC, Henry EA, Mitchell R (1992) Sulfate stimulation of mercury methylation in freshwater sediments. Environ Sci Technol 26:2281–2287

Gilmour CC, Riedel GS (2000) A survey of size-specific mercury concentrations in game fish from Maryland fresh and estuarine waters. Arch Environ Contam Toxicol 39:53–59

Greenfield BK, Davis JA, Fairey R, Roberts C, Crane DB, Ichikawa G, Petreas M (2003) Contaminant concentrations in fish from San Francisco Bay, 2000. SFEI Contribution # 77, San Francisco Estuary Institute, July 2003

Griffin JC, Margraf FJ (2003) The diet of Chesapeake bay striped bass in the late 1950s. Fish Manage Ecol 10:323–328

Heyes A, Mason RP, Kim E-H, Sunderland E (2005) Mercury methylation in estuaries. Mar Chem (in press)

Heyes A, Miller C, Mason RP (2004) Mercury and methylmercury in Hudson River Sediment: Impact of resuspension on portioning and methylation. Mar Chem 90:75–89

Hildebrand SF, Schroeder WC (1928) Fishes of Chesapeake Bay. Bulletin of the Bureau of Fisheries, pp 242–251

Holsbeek L, Das HK, Joiris CR (1997) Mercury speciation and accumulation in Bangladesh freshwater and anadromous fish. Sci Tot Environ 198:201–210

Hudson RJM, Gherini SA, Watras CJ, Porcella DP (1994) Modeling the biogeochemical cycle of mercury in lakes: The mercury cycling model (MCM) and its application to the MTL study lakes. In: Watras CJ, Huckabee JW (eds) Mercury pollution: integration and synthesis. Lewis Publishers, Boca Raton, Florida, pp 473–526

Hudson River Foundation (HRF) (2004) Health of the harbor: The first comprehensive look at the state of the NY/NJ harbor estuary. http://www.harborestuary.org/reports/harborhealth.pdf

Kannan K, Smith RG, Lee RF, Windom HL, Heitmuller PT, Macauley JM, Summers JK (1998) Distribution of total mercury and methyl mercury in water, sediment, and fish from south Florida estuaries. Arch Environ Contam Toxicol 34:109–118

Kim EY, Saeki K, Tanabe S, et al. (1996) Specific accumulation of mercury and selenium in seabirds. Environ Poll 94:261–265

Kraus RT, Secor DH (2004) Incorporation of strontium into otoliths of an estuarine fish. J Exper Mar Biol Ecol 302:85–106

Lawrence AL, Mason RP (2001) Factors controlling the bioaccumulation of mercury and methylmercury by the estuarine amphipod *Leptocheirus plumulosus*. Environ Poll 111:217–231

Lawerence AL, McAloon KM, Mason RP, Mayer LM (1999) Intestinal solubilization of particle-associated organic and inorganic mercury as a measure of bioavailability to benthic invertebrates. Environ Sci Technol 33:1871–1876

Mansueti RJ (1961) Age, growth, and movements of the striped bass, *Roccus saxatilis*, taken in size selective fishing gear in Maryland. Ches Sci 2:9–36

Mason RP (2002) The bioaccumulation of mercury, methylmercury and other toxic elements into pelagic and benthic organisms. In: Newman MC, Robert MH, Hale RC (eds) Coastal and estuarine risk assessment. CRC/Lewis Publishers, pp 127–149

Mason RP, Benoit JM (2003) Organomercury compounds in the environment. In: Craig P (ed) Organometallics in the environment. John Wiley & Sons, New York, pp 57–99

Mason RP, Fitzgerald WF (1996) Sources, sinks and biogeochemical cycling of mercury in the ocean. In: Baeyens W, Ebinghaus R, Vasiliev O (eds) Global and regional cycles of mercury: sources, fluxes and mass balances. Kluwer Academic Publishers, Dordrecht, the Netherlands, pp 85–108

Mason RP, Fitzgerald WF, Morel FM (1994) The biogeochemical cycling of elemental mercury: anthropogenic influences. Geochim Cosmochim Acta 58:3191–3198

Mason RP, Lawrence AL (1999) Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore Harbor and Chesapeake Bay, Maryland, USA. Environ Toxic Chem 18:2438–2447

Mason RP, Lawson NM, Lawrence AL, Lee JG, Leaner JJ, Sheu G-R (1999) Mercury in the Chesapeake Bay. Mar Chem 65:77–96

Mason RP, Lawson NM, Sheu G-R (2000) Annual and seasonal trends in mercury deposition in Maryland. Atmos Environ 34:1691–1701

Mason RP, Lawson NM, Sullivan KA (1997) Atmospheric deposition to the Chesapeake bay watershed: regional and local sources. Atmos Environ 31:3531–3540

Mason RP, Reinfelder JR, Morel FM (1996) Uptake, toxicity and trophic transfer of mercury in a coastal diatom. Environ Sci Technol 30:1835–1845

Mason RP, Sheu G-R (2002) The role of the ocean in the global mercury cycle. Global Biogeochemical Cycles, 16(4), 1093, doi:10.1029/2001GBC001440

Mason RP, Sveinsdottir AY (2003) Mercury and methylmercury concentrations in water and largemouth bass in Maryland reservoirs. Final report submitted to Maryland Department of Natural Resources, CBWP-MAN7A-AD-03-1. Also a paper on this topic is currently in review for Arch Environ Contam Toxicol

MDE (2004) Maryland Department of the Environment Mercury Website. http://www.mde.state.md.us/Programs/LandPrograms/Hazardous-Waste/Mercury

Morel FMM, Kraepiel AML, Amyot M (1998) The chemical cycle and bioaccumulation of mercury. Ann Review Ecol Systematics 29:543–566

Murdy EO, Birdsong RS, Musick JA (1997) Fishes of the Chesapeake Bay. Smithsonian Institution Press, Washington and London, pp 216–244

National Oceanographic and Atmospheric Administration (NOAA) (2003) Commercial and recreational fish of the Chesapeake Bay. http://noaa.chesapeakebay.net/species.htm

Riget F, Asmund G, Aastrup P (2000) Mercury in Arctic char (*Salvelinus alpinus*) populations from Greenland. Science Total Environ 245:161–172

Rochelle-Newall EJ, Fisher TR (2002) Chromophoric dissolved organic matter and dissolved organic carbon in Chesapeake Bay. Mar Chem 77:23–41

Rodgers DW (1994) You are what you eat and a little bit more: bioenergetics-based models of methylmercury accumulation in fish revisited. In: Watras CJ, Huckabel JW (eds) Mercury pollution: integration and synthesis. Lewis Publishers, New York, pp 427–439

Rolfhus KR, Fitzgerald WF (1995) Linkages between atmospheric mercury deposition and the methylmercury content of marine fish. Water Air Soil Poll 80:291–297

Rudd JWM (1995) Sources of methylmercury to freshwater ecosystems: A review. Water Air Soil Poll 80:697–713

Secor DH, Rooker JR, Zlokovitz E, Zdanowicz VS (2001) Identification of riverine, estuarine, and coastal contingents of Hudson River striped bass based upon otolith elemental fingerprints. Mar Ecol Prog Ser 211:245–253

Sheu G-R, Mason RP, Lawson NM (2002) Speciation and distribution of atmospheric mercury over the Northern Chesapeake Bay. In: Lipnick RL, Mason RP, Phillips ML, Pittman CU Jr, (eds) Chemicals in the environment: fate, impacts, and remediation. American Chemical Society Publishers, ACS symposium series no. 806, pp 223–242

Sveinsdottir AY (2002) Methylmercury in largemouth bass (Micropterus salmoides) and forage fish from Maryland reservoirs and factors influencing uptake. Masters Thesis. University of Maryland, Chesapeake Biological Laboratory

Sveinsdottir AY, Mason RP (2005) Factors controlling mercury and methylmercury concentrations in largemouth bass (*Micropterus salmoides*) and other fish from Maryland reservoirs. Arch Environ Contam Toxicol 49:528–545

US Environmental Protection Agency (USEPA) (1995) National listing of fish consumption advisories. USEPA, EPA-823-F-95-004, Office of Water, Washington, DC

USEPA (2004) Fish consumption advice webpage. http://www.epa.gov/waterscience/fishadvice/advice.html

US Federal Drug Administration (USFDA) (2002) Consumer advisory: an important message for pregnant women and women of childbearing age who may become pregnant about the risks of mercury in fish. http://vm.cfsan.fda.gov/~dms/ admehg.html

U.S. Geological Service (USGS) Website (2004) http://md.water.usgs.gov/

Wagemann R, Trebacz E, Boila G, et al. (1998) Methylmercury and total mercury in tissues of arctic marine mammals. Sci Tot Environ 218:19–31

Walter JF, Austin HM (2003) Diet composition of large striped bass (*Morone saxatilis*) in Chesapeake Bay. Fish Bull 101:414–423

Watras CJ, Bloom NS (1992) Mercury and methylmercury in individual zooplankton. Liminol Oceanog 37:1313–1318

Watras CJ, Bloom NS, Hudson RJM, Gherini S, Munson R, Claas SA, Morrison KA, Hurley J, Wiener JG, Fitzgerald WF, Mason RP, Vandal G, Powell D, Rada R, Rislov L, Winfrey M, Elder J, Krabbenhoft D, Andren AW, Babiarz C, Porcella DB, Huckabee JW (1994) Sources and fates of mercury and methylmercury in Wisconsin lakes. In: Watras CJ, Huckabee JW (eds) Mercury pollution: integration and synthesis. Lewis Publishers, Boca Raton, Florida, pp 153–177

Weiss J, Trip L, Mahaffey KR (1999) Methylmercury: a new look at the risks. Public Health Reports 114:397–401

Wiener JG, Krabbenhoft DP, Heinz GH, Scheuhammer AM (2002) Ecotoxicology of mercury. In: Hoffman DJ, Rattner BA, Burton GA Jr, Cairns J Jr, (eds) Handbook of ecotoxicology, 2nd ed. CRC Press, Boca Raton, Florida, pp 409

Wolfe MF, Schwarzbach S, Sulaiman RA (1998) The effects of mercury on wildlife: a comprehensive review. Environ Toxicol Chem 17:146

World Health Organization (1990) Environmental health criteria 101: Mercury I. Geneva, pp 144